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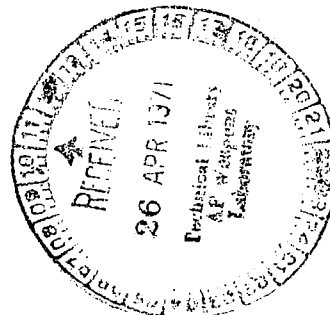
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**PERFORMANCE CHARACTERISTICS OF
A THERMIONIC CONVERTER WITH A (110)
TUNGSTEN EMITTER AND A COLLECTOR OF
NIOBIUM WITH TRACE AMOUNTS OF TUNGSTEN
AND NIOBIUM CARBIDE ON THE SURFACE**

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Prepared by
GENERAL ELECTRIC COMPANY
Schenectady, N. Y.
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16. Abstract A parallel plane, variable spaced converter with a tungsten emitter having the (110) planes parallel to the surface and a niobium collector was fabricated. The performance of this converter was mapped for various emitter, collector, and cesium reservoir temperatures and is compared to the performance of a converter having a tungsten (110) emitter and a nickel collector. At low temperatures (emitter temperature = 1673° K), the performance of the two converters is comparable. At higher temperatures, the performance of the tungsten (110) niobium converter is lower than the tungsten (110) nickel converter. The output increased during the first five hours of operation, but after that remained constant for about 100 hours of intermittent operation.					
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FOREWORD

The research described in this report was conducted by the General Electric Company under NASA contract NAS 3-8511 with R. P. Migra of the Lewis Research Center Nuclear Systems Division as the NASA Project Manager. The report was originally issued as General Electric report GESP-9005.

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SUMMARY

Performance tests were made on a parallel plane variable spaced converter. The emitter had a chloride vapor deposited tungsten (CVD-W) layer 0.020-inch thick which was polycrystalline but with almost perfect preferred orientation with the (110) crystal planes parallel to the bulk surface. The collector was polycrystalline niobium (Nb). Before assembling the converter, the vacuum work function of the emitter was 4.95 electron volts (eV) at 2200°K. After assembly and outgassing, it measured 4.99 eV. After admitting the cesium (Cs), but before operating the converter, the minimum work function of the collector was 1.43 eV. This value is low for Cs on Nb. When the converter was taken apart after operation, the collector had a thin coating of elemental W plus a small amount of niobium carbide (NbC). It is believed that C originated from converter contamination and W originated from the emitter. Cesium on W probably gave the low work function value of the collector.

At an emitter temperature (T_E) of 1673°K, the output power of this converter was comparable with the output of a converter previously measured which had an identical emitter, but a nickel (Ni) collector. However, with increasing emitter temperatures, the output of the W(110)-Nb converter progressively developed less output power than the W(110)-Ni converter. Comparing the J-V curves from the two converters suggests that the difference in output is due to collector work function differences. For some unknown reason, the work function of Nb covered with Cs is higher than for Ni at the higher Cs pressures and for the range of collector temperatures studied--850 to 1125°K.

After measuring the output at $T_E = 1673, 1770, 1865$ and 1963°K, the measurements at 1673 were repeated. These J-V

curves agree with the first set taken; therefore, a degradation with time of the W(110)-Nb converter did not occur. A complete set of data from $T_E = 1673$ to 2153°K was taken. Up to 1963°K these data reproduced the original set.

Based on light microscope observations of etch pits and facets, x-ray diffraction and vacuum work function measurements, the two emitters appear very nearly identical. However, the emitter used with the Ni collector gave a little more electron emission under identical conditions of T_E and T_{CS} .

A number of measurements of the electron emission from the collector were made at a collector temperature (T_C) of about 800°K . These were made before operating, after operating for about 25 hours and extensively after 100 hours of operation to take the families of J-V curves. From these measurements, one could calculate the collector work function for a Richardson-Dushman constant of 120. From these values, the collector work function appeared to vary with time at room temperature and with time at normal operating collector temperature. However, judging by the J-V curves the collector work function reached an equilibrium value after an hour or two of steady operating conditions.

INTRODUCTION

This work is part of a continuing program to build and operate thermionic converters with various electrode materials in order to characterize, evaluate, and identify the most promising electrode surfaces for converter operation. The design of the test converter was standardized in 1963. It permitted an accurate determination of the electrode spacing and used a guard ring to accurately define the converter area. The guard ring could be kept at the same temperature and potential as the collector. The first six lines of Table 1 list the electrode materials and the spacings for six converters built according to the 1963 design. The output power for these converters was consistently high and variations in output power could be explained by variations in electrode surfaces. The emitters of these converters were pre-heated to 2500°C for a half hour and all other parts of the converter were heated at least 100°C hotter during processing than the operating temperature for each part.

In 1966, under NASA sponsorship, the program was altered in two respects: (1) a more elaborate converter was built so that the electrode spacing of each converter could be varied, and (2) a much more intensive program to characterize the emitters was inaugurated. The NASA program, covered by Task III of Contract NAS 3-8511, began with the first variable-spaced diode tested--namely, item 7 of Table 1. This report presents the emitter and collector preparation and the test results for the vapor deposited (110) W emitter and Nb collector in a variable-spaced converter (item 10 of Table 1). The test results are documented in the references listed in the table.

TABLE 1

		<u>Collector</u>	<u>Spacing (Inches)</u>
(1)	Polycrystalline Tungsten ⁽¹⁾	Ni	0.005
(2)	Polycrystalline Rhenium ⁽¹⁾	Ni	0.005
(3)	Polycrystalline Rhenium ^(2, 3, 4)	Ni	0.002
(4)	Polycrystalline Tungsten ^(4, 5)	Ni	0.002
(5)	Polycrystalline Tungsten ⁽⁵⁾	W	0.002
(6)	Tungsten-25 weight percent Rhenium ⁽⁶⁾	Ni	0.005
(7)	Polycrystalline Tungsten ^(7, 8)	Nb	0.001 to 0.020*
(8)	Vapor Deposited (100) Tungsten (110) Etch ⁽⁹⁾	Nb	0.001 to 0.020
(9)	Vapor Deposited (110) Tungsten ⁽¹⁰⁾	Ni	0.005
(10)	Vapor Deposited (110) Tungsten	Nb	0.002 to 0.020
(11)	Vapor Deposited (112) to (114) Tungsten**	W+WO ₂ on Nb	0.002 to 0.020
(12)	Vapor Deposited (110) Tungsten**	Mo on Nb	0.005 to 0.020

* This converter did not have a guard ring.

** Report to be published.

The vapor deposited W(110) was electropolished to expose the $\{110\}$ planes which appear to be the most stable and the most reproducible emitter surface. The converter of this report used such an emitter surface with a Nb collector. By comparing the output of this converter with the output of a converter with an identical emitter but with a Ni collector, one can compare the relative performance of Nb and Ni as collector materials.

THE TEST VEHICLE

Figure 1 shows a cross section drawing of the thermionic converter. It is identical to the converter of the previous investigation and is a parallel plane converter with variable spacing. The guard and collector may be maintained at the same temperature and the same potential.

PREPARATION OF THE EMITTER

The emitter was a disk of General Electric weldable grade tungsten 1 inch in diameter and 1/4-inch thick coated with a 0.020-inch-thick layer of (110) oriented W by a chloride chemical vapor deposition. Of the five emitter blanks, two had crystal orientations with the (110) planes very nearly parallel to the bulk surface. After mechanically polishing and electropolishing, these two samples were heat treated in vacuum for a half hour or more at 2500°C and the work function of each sample was measured by thermionic emission in vacuum. The emitter used with the Ni collector had a work function (ϕ_E) of 4.96 eV at 2200°K. The ϕ_E used with the Nb collector (subject converter of this report) was 4.95 eV at 2200°K. Figure 2 shows work function measurements after assembling and outgassing the converter.

COLLECTOR WORK FUNCTION

Figure 3 shows the work function of the collector as a function of the ratio of T_C/T_{Cs} . The dots and crosses were made at collector temperatures (T_C) of about 780°K and 810°K, respectively. The minimum work function is about the same as for Cs on Ni. For comparison, Figure 4 is a reproduction of Figure 3 of NASA CR-1033. Notice that the minimum work function for Cs on Nb, in this case, is 1.54 eV, whereas in Figure 3 it is 1.43 eV. When the converter was taken apart at the conclusion of

the tests, it was discovered that a film of W and a trace of NbC was on the collector. Presumably these films were deposited during the high temperature outgassing of the converter.

A general discussion of the work function of cesiated surfaces may be in order. The lower values given in Figures 3 and 4 are probably the result of traces of oxygen on the collector surfaces. Since in thermionic converters it is impossible to flash the collectors to high temperatures, it is impossible to get the surfaces atomically clean. Nickel forms an oxide layer on the surface. In general, the work functions of oxides are higher than for the corresponding clean metals. Furthermore, the higher the work function of a base material is, the lower is the work function of the corresponding cesiated surface. Cesium work functions from 1.36 to 1.43 eV have been measured. These were probably Ni-O-Cs surfaces. At the collector operating temperature, Nb does not form oxide surface layers but rather oxygen is dissolved into the metal. Therefore, it is improbable that a Nb-O-Cs surface is formed. The low ϕ_C value in Figure 3 is possibly ϕ_C for a W-O-Cs surface. Cesium NbC would have a high work function; therefore, the trace of NbC apparently did not influence ϕ_C appreciably.

OUTPUT CHARACTERISTICS

The minimum value of ϕ_C of 1.43 eV for this converter, shown in Figure 3, suggests that the output voltage should be similar to the output voltage for a converter with a similar emitter and a Ni collector. The open circle at the left of Figure 5 represents the output for one of the first runs. Indeed, the output is as expected.

However, as T_E was increased, the output did not follow the output of the W(110)-Ni converter but became progressively lower. This is indicated by the open circles. The collector work function was remeasured to see if the converter was changing its characteristics. These data are shown by the open circles of Figure 3; ϕ_{min} was still 1.43 eV. The crosses of Figure 5 represent selected points from a complete set of J-V curves which are given in the Appendix. Apparently the converter was not changing with time of operation, but for some reason as T_E is increased this converter produces less output voltage than does the Ni collector converter.

A difference in work function of the collector shows up in the J-V curves as a difference in output voltage, particularly at the lower current densities (from 5 to 10 amperes/cm²). From Figures 6, 7, and 8, it appears that the relative improvement with increasing T_E of the converter with the Ni collector is primarily due to a relatively lower collector work function.

Also in Figures 6, 7, and 8 it may be noticed that to match the current densities of the two W(110) emitters at $V=0$, one would need to operate the W(110)-Nb converter at a Cs reservoir temperature about 10°K higher than that for the W(110)-Ni converter. By visual observations in a microscope, by x-ray diffraction, and by work function measurements, these two emitters appear very nearly identical; however, the emitter used with the Ni collector appears to give a little more electron emission under identical conditions of T_E and T_{Cs} . This difference is believed to be a difference in the outgassing. Possibly the converter with the Ni collector contained an extremely small amount more of O₂ than the other converter. Perhaps the Nb collector acts as a getter to clean up the O₂;

however, it is more probable that the entire procedure for assembly, outgassing and introducing the Cs needs to be improved before perfect reproducibility from one converter to another can be achieved. This observed difference in these two converters could be caused by a difference of a very small fraction of a monolayer of Cs coverage on the two emitters.

Four days after taking the complete set of J-V curves given in the Appendix which required about 100 hours of operation, the work function of the collector was measured at $T_C = 800^\circ\text{K}$ and at increasing T_{Cs} values. The first run is shown as solid circles in Figure 9. For comparison the data taken after 25 hours of converter operation are shown as open circles. A second run at $T_C = 800^\circ\text{K}$ seemed to change ϕ_C . A single measurement was made on January 6, 1969, about two weeks later. This showed a work function of 1.66 eV. These measurements spanned about three weeks and during this interval the converter was not operated. The emitter was heated occasionally to about 900°K and the collector to 800°K . It is apparent that the work function of the collector did not remain constant. Although these data are plotted as a function of T_C/T_{Cs} , the ratio is very suspect. At low collector and emitter temperatures, it is not certain that there is not a cool part of the converter that may act as a secondary reservoir and give an effective T_{Cs} lower than measured and used to calculate the quoted T_C/T_{Cs} . Thus, the points for high values of T_C/T_{Cs} are taken for very low values of T_{Cs} . Cesium coming from surfaces inside the converter may give a Cs pressure between the electrodes higher than would be at equilibrium with the liquid Cs at T_{Cs} . Thus, the points to the right may be plotted for too high values of T_C/T_{Cs} .

Although one should not consider seriously the shape of these curves, it appears certain that the work function of the collector varied with time and with a heat treatment as low as 800°K. During this time, ϕ_C was increasing and approached a value consistent with a ϕ for Cs on a pure refractory metal.

The converter was then operated for five hours on January 9, 1969, at T_E values from 1770 to 1962°K, T_{Cs} values of 593 and 613°K, and T_C value of 998°K. Figure 10 shows the J-V curve change in this 5-hour interval. The dashed curve of Figure 10 is a reproduction of a curve from Figure A-10 taken earlier in the testing program. Notice that the converter initially had low output voltage at 5 and 10 Amps/cm²; but during the 5 hours of operation, the output voltage increased about 0.2 eV.

The next day, ϕ_C was measured again. These data are shown as squares in Figure 9. The numbers 1 to 4 indicate the order in which the points were taken. Apparently ϕ_C was increasing while taking the ϕ_C measurements. That is why no curve was drawn through these points.

One may speculate that at the beginning of the 5-hour run, ϕ_C was 1.66 eV but decreased during the run to about 1.46 eV. The next day it had increased to about 1.58 eV and increased still further as ϕ_C measurements represented by the squares were taken.

These ϕ_C measurements were not made at the collector operating temperature, but at about 200° C lower. Considerable work has been done in this laboratory and at the Thermo Electron Engineering Company to develop a method for measuring ϕ_C at operating conditions and during operation. Back emission and retarding plot techniques are confused by heavy electrical discharges.

Because ϕ_C cannot be measured under operating conditions and because ϕ_C appears to change with time at room temperature, the plots of ϕ_C versus T_C/T_{Cs} are confusing and difficult to interpret. Probably the best way to infer ϕ_C at operating conditions is from the output voltage of the converter at about 5 amperes/cm².

CONDITION OF THE ELECTRODES AFTER OPERATION

When the converter was opened, the emitter was very clean and showed large grains about 2 mm in diameter. An x-ray analysis of the emitter gave only one strong reflection as though it were a single crystal with the (110) planes parallel to the bulk surface; so the emitter had not changed its surface structure.

The collector had a thin dark deposit. Just enough to give the mirror surface a slightly cloudy appearance. An x-ray diffraction analysis revealed that this was elemental W plus a smaller amount of NbC.

Since the first work function measurement gave an unusually low value for Cs on Nb, probably W and NbC were present throughout the tests. Some W was deposited during the outgassing and ϕ_E measurements. The presence of C must reflect a lack of adequate cleanliness in assembling the converter.

CONCLUSIONS

This converter with a W(110) emitter and a Nb collector developed progressively less output power with increasing T_E than a similar converter with a Ni collector. The collector had a thin coating of elemental W and a trace amount of NbC. Since it is impossible to completely remove oxygen from a converter, the actual collecting surface was probably W with a monolayer of O₂

covered with Cs. A trace of NbC was also present, but apparently did not affect the operation of the converter. It is believed that the source of the W was the emitter and the C was a contamination that is difficult to avoid. Therefore, the output power from this converter may be representative of the output to expect from W(110)-Nb converters, when processed according to present techniques.

It is concluded from the results of this test device that more work needs to be done to improve the cleaning, outgassing and Cs filling of converters. Following this effort, it would be desirable to test for reproducibility to be sure that the results are not influenced by some uncontrolled variable such as minor contaminations. It is recognized, however, that such a testing effort would represent a fairly extensive development program.

A minimum ϕ_C of 1.43 eV was observed. This value is low for Cs on Nb and suggests the presence of the W-O-Cs surface on the Nb. Variations of ϕ_C were observed when the collector was at room temperature or at 800°K but the emitter was cold. With normal operation of the converter, within a few hours ϕ_C returned to a reproducible value, judging from the converter output voltage.

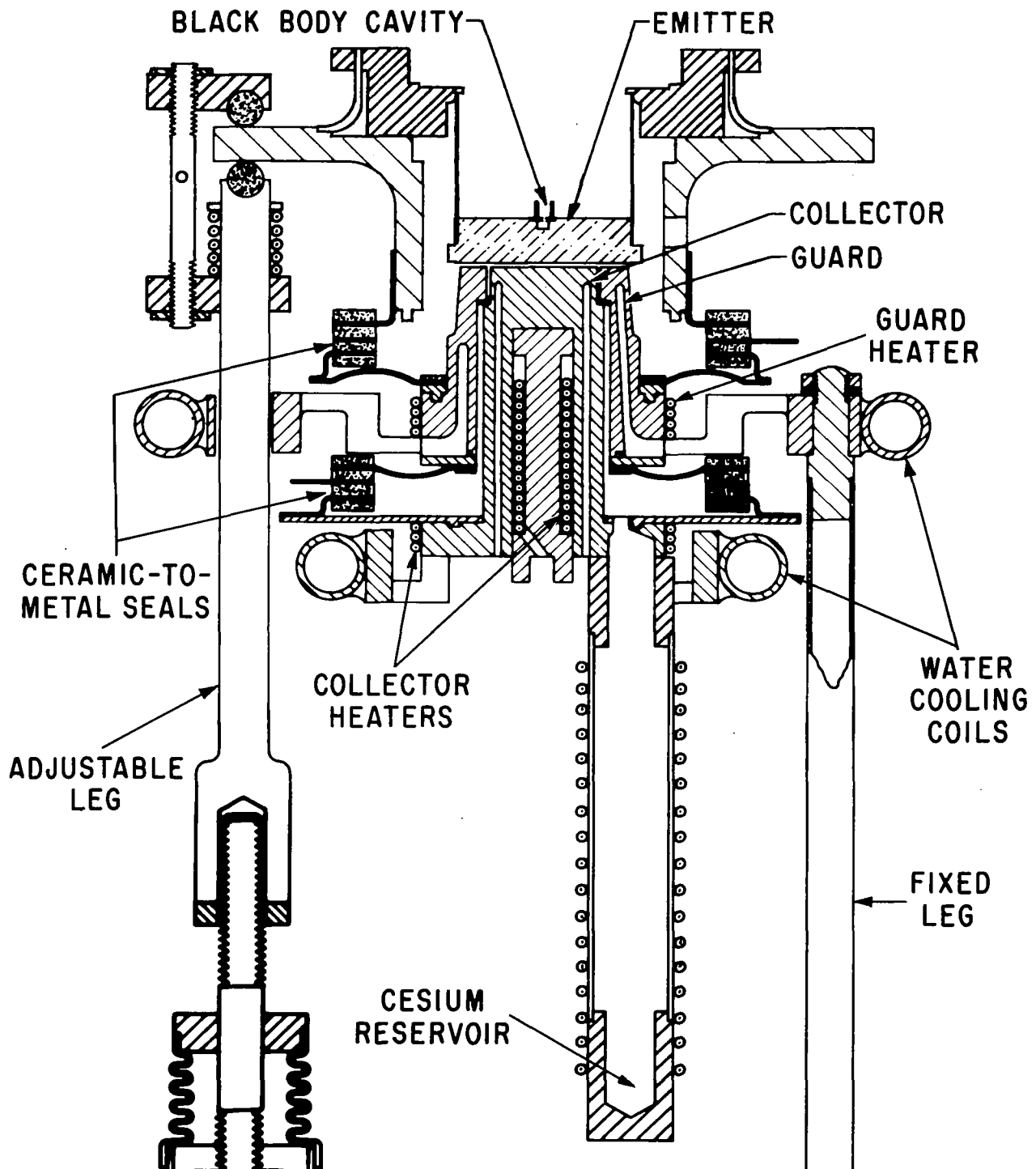


Figure 1. CROSS SECTION OF THE THERMIONIC CONVERTER

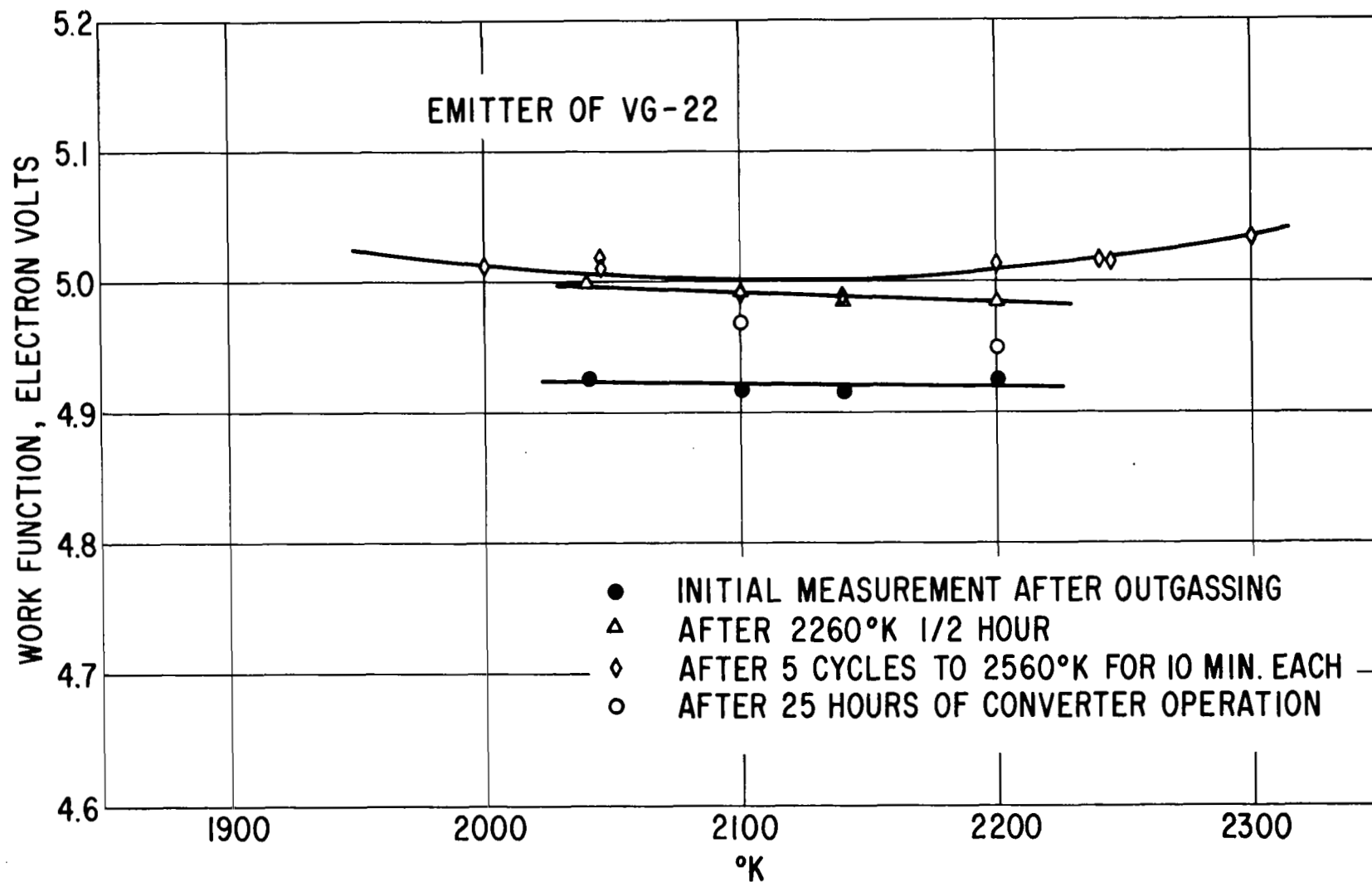


Figure 2. EMITTER WORK FUNCTION VERSUS EMITTER TEMPERATURE AT VARIOUS STAGES OF PROCESSING AND OPERATION

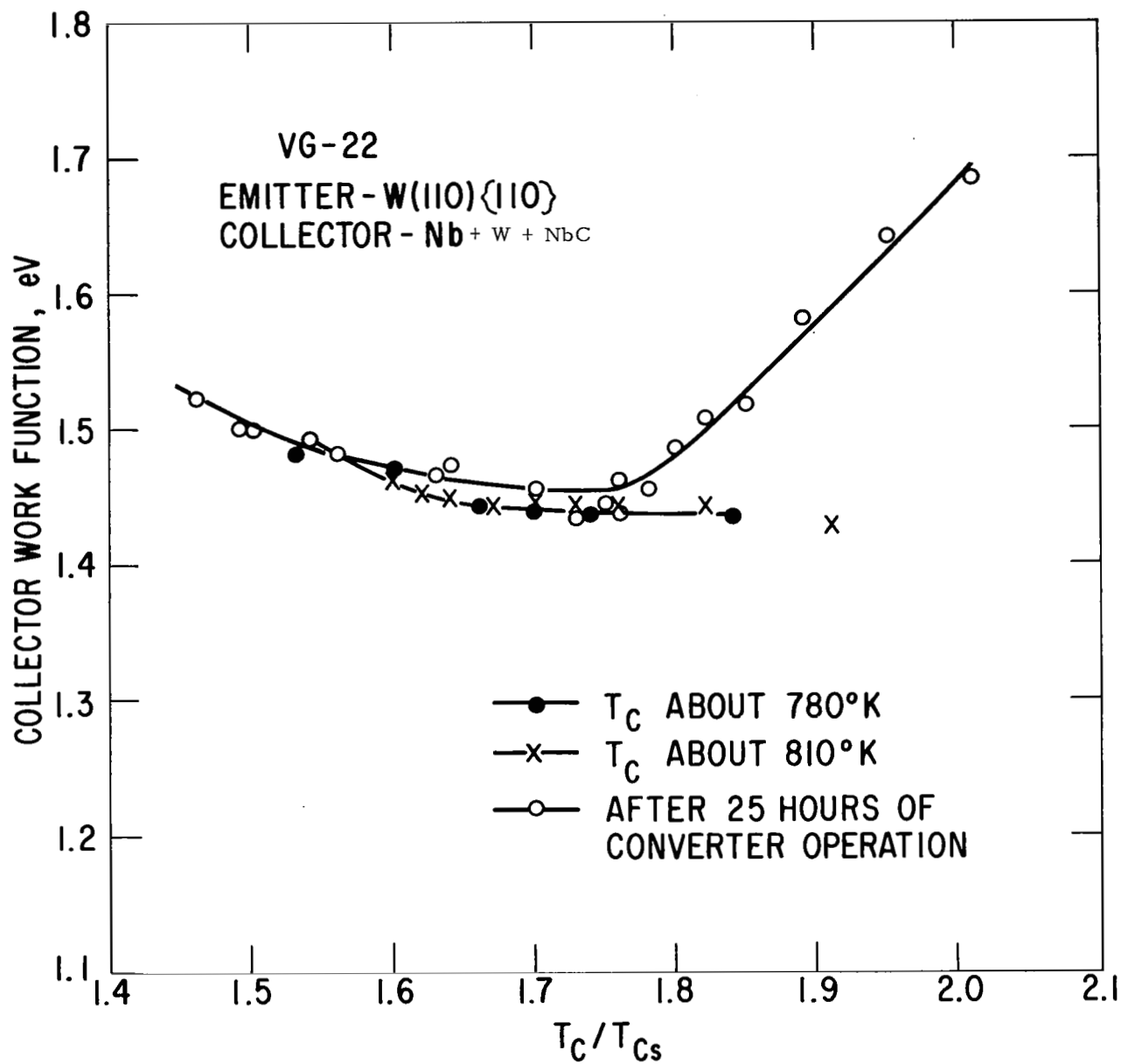


Figure 3. COLLECTOR WORK FUNCTION VERSUS T_C/T_{Cs}
 (T_C/T_{Cs} values are suspect--see pages 6 and 7).

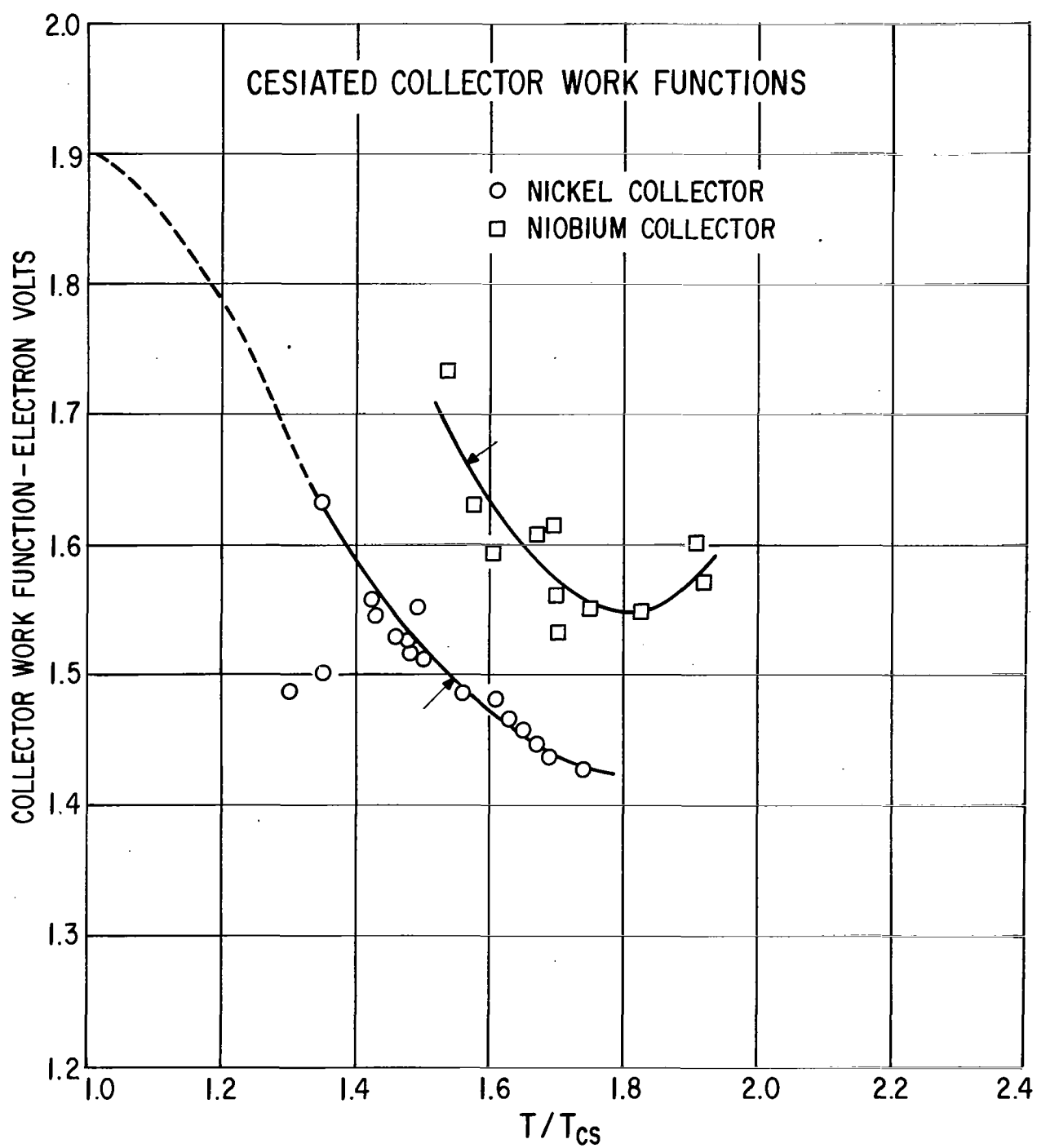


Figure 4. COLLECTOR WORK FUNCTION VERSUS T_C/T_{Cs}

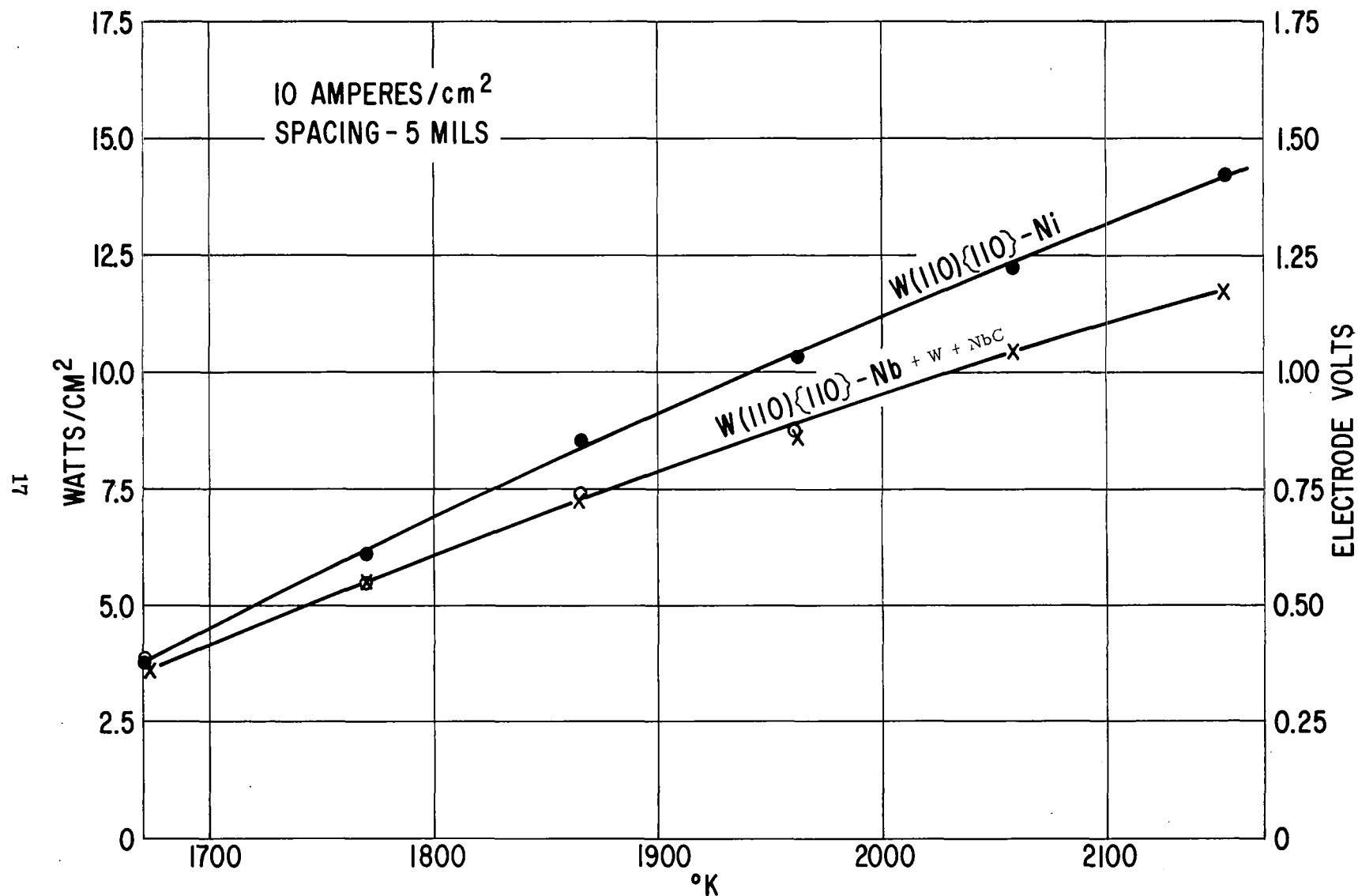
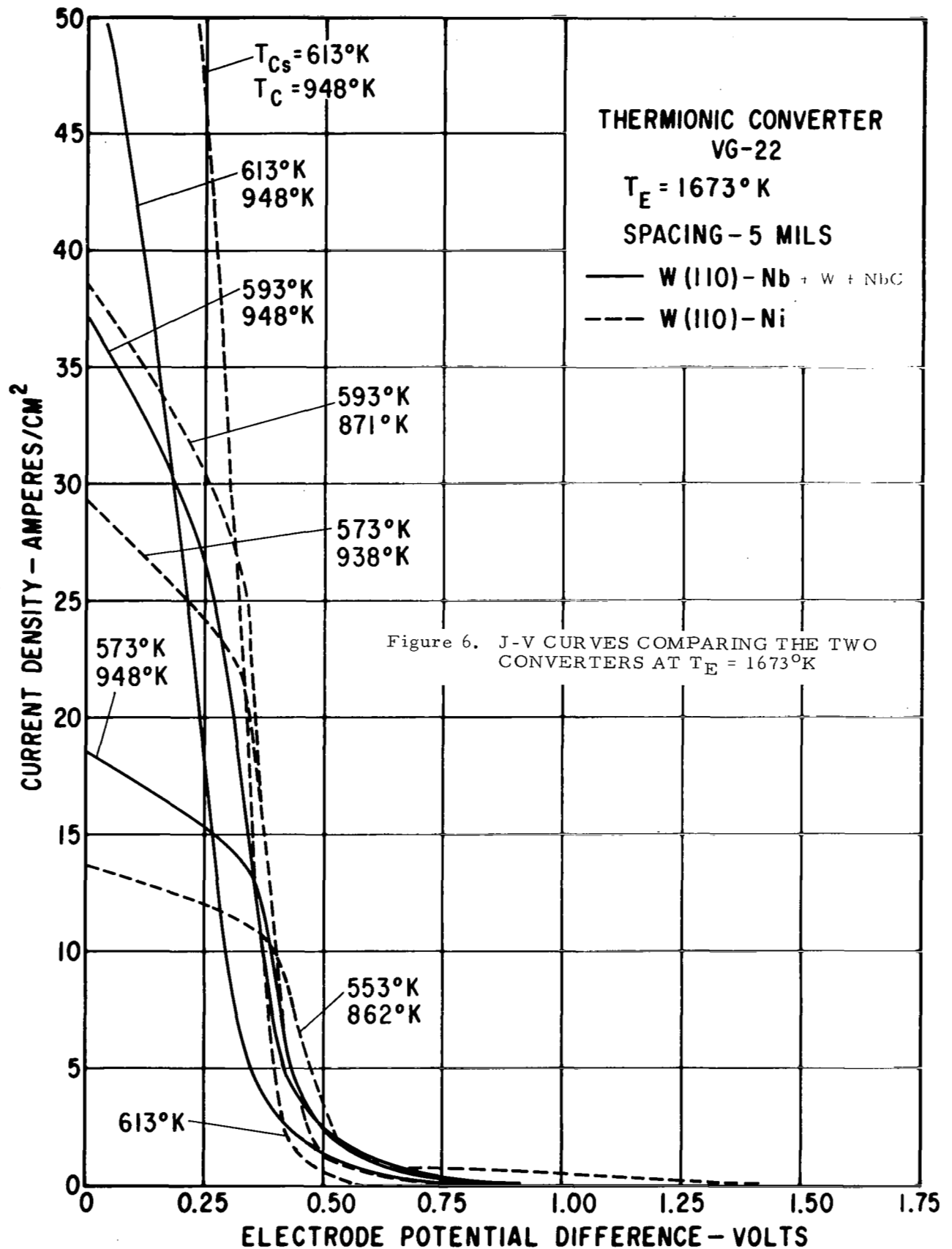
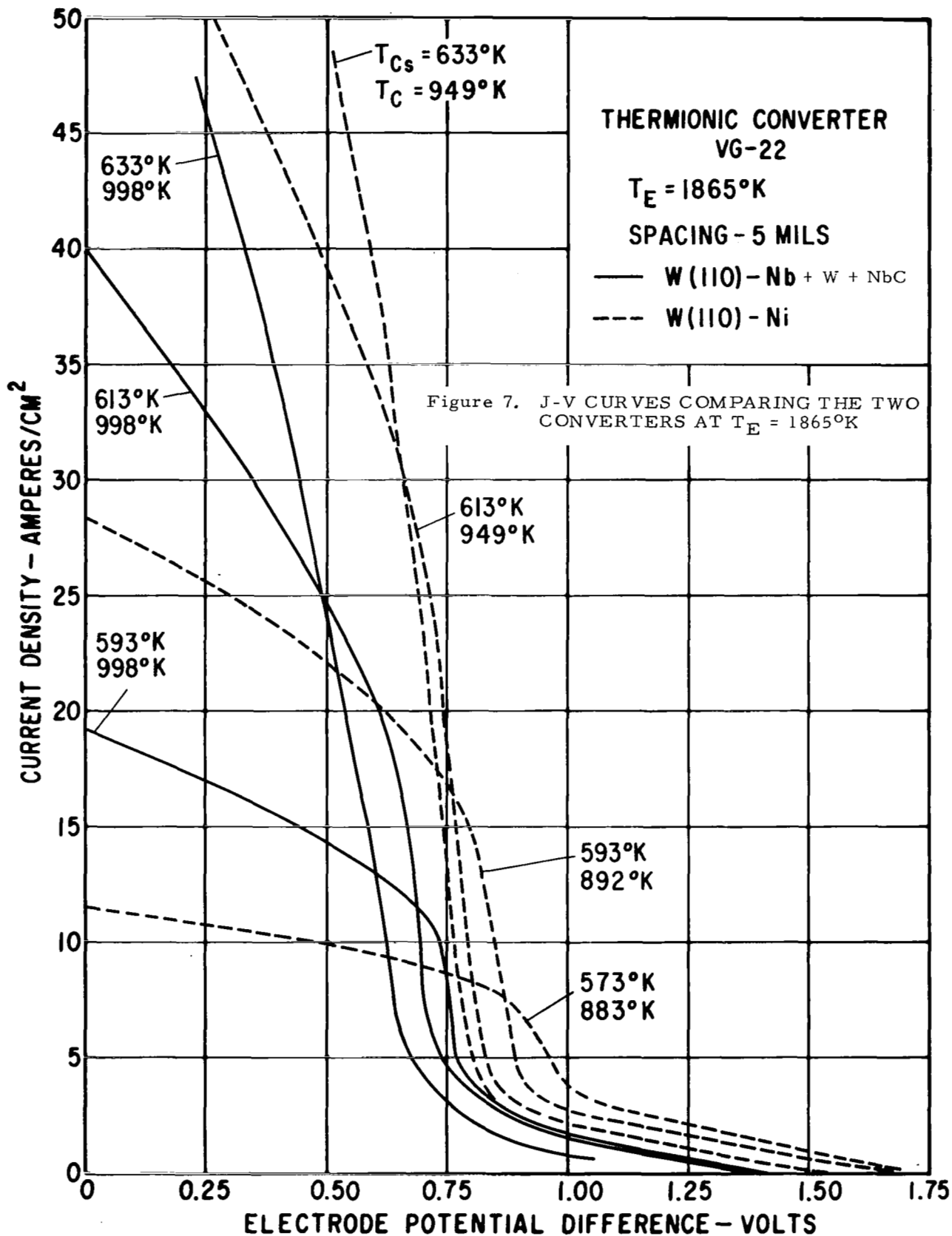
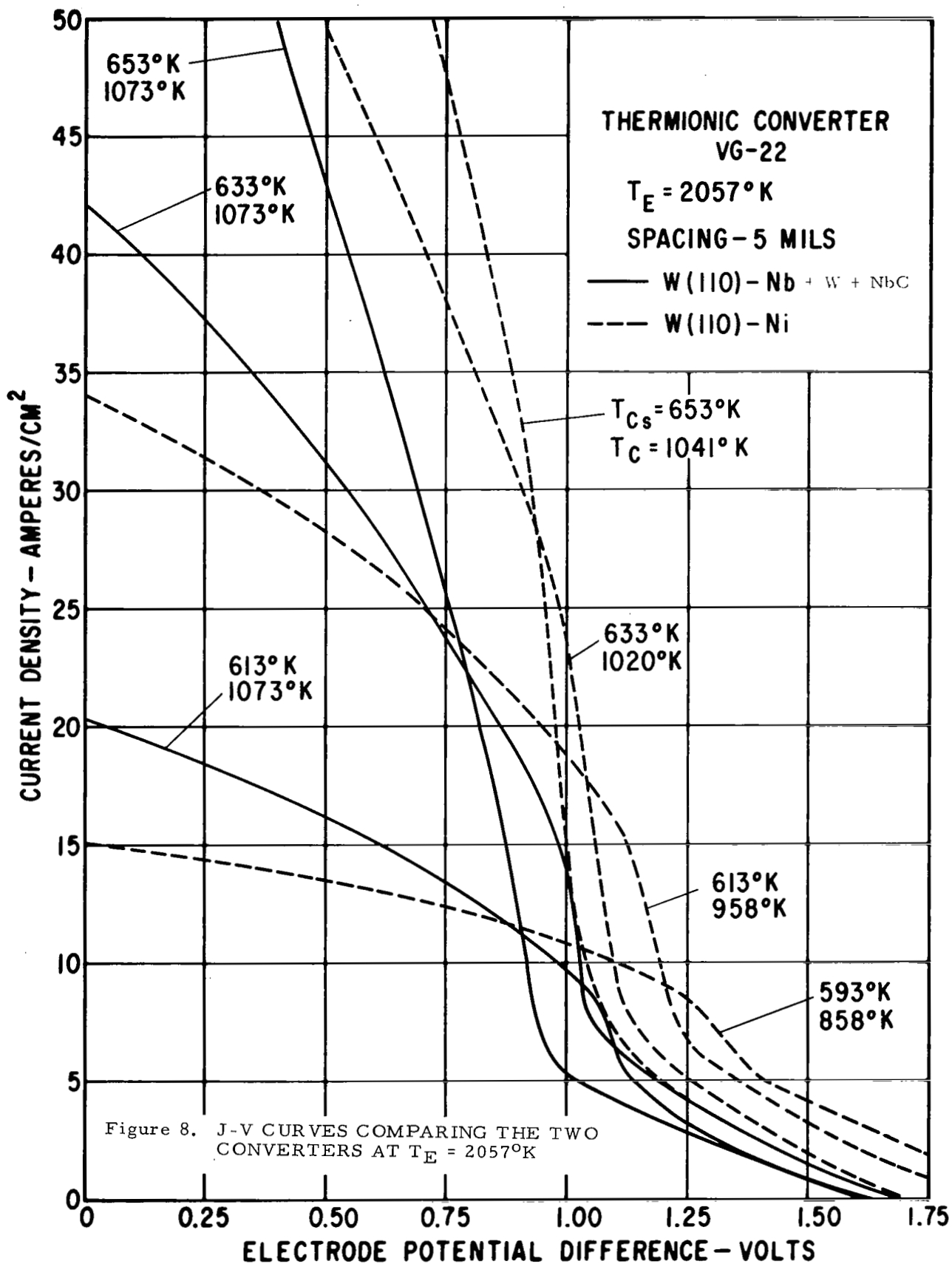


Figure 5. COMPARISON OF THE OUTPUT POWER VERSUS T_E FOR TWO CONVERTERS WITH SIMILAR EMITTERS - ONE HAS A Ni COLLECTOR, THE OTHER A Nb COLLECTOR







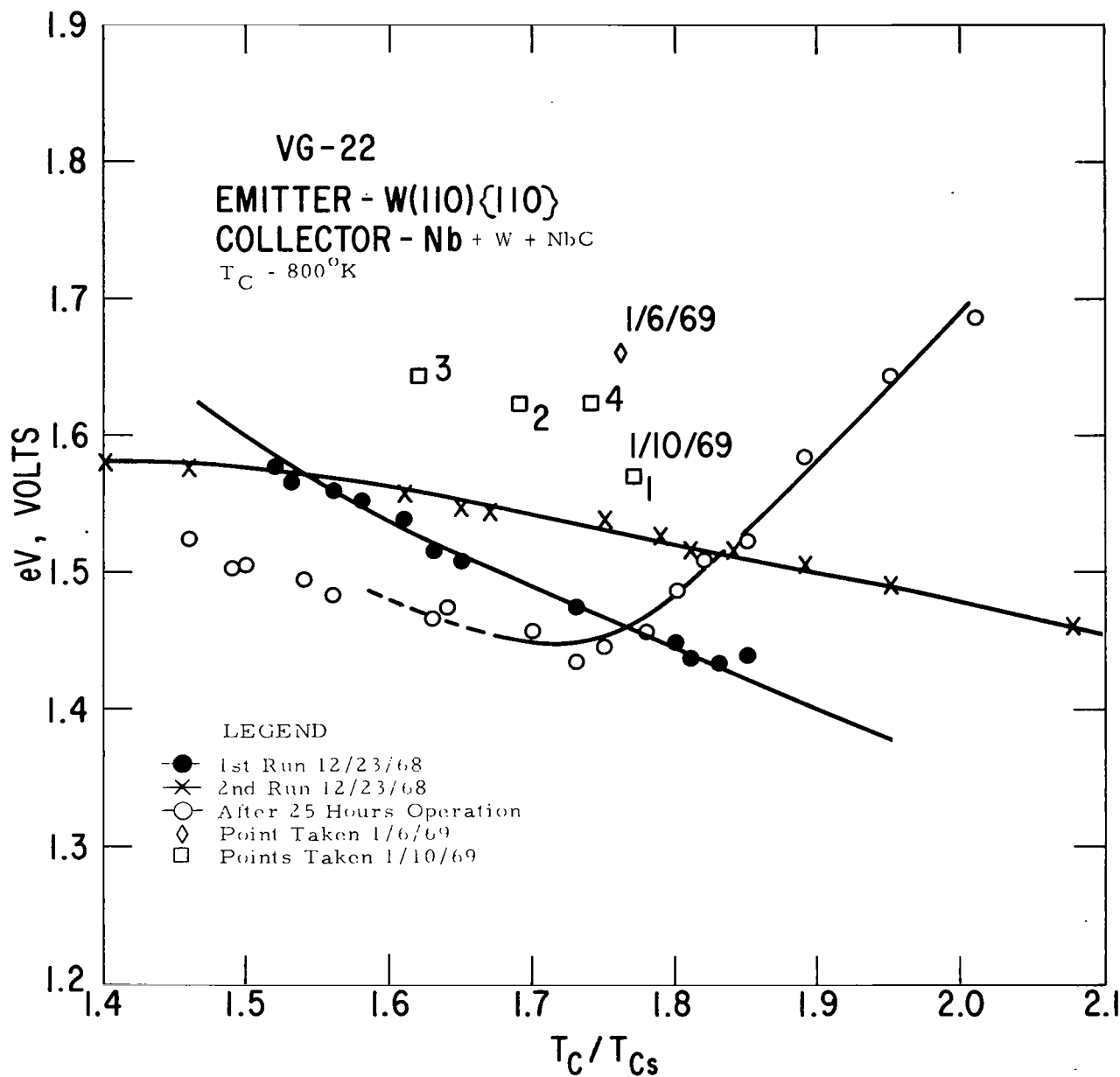
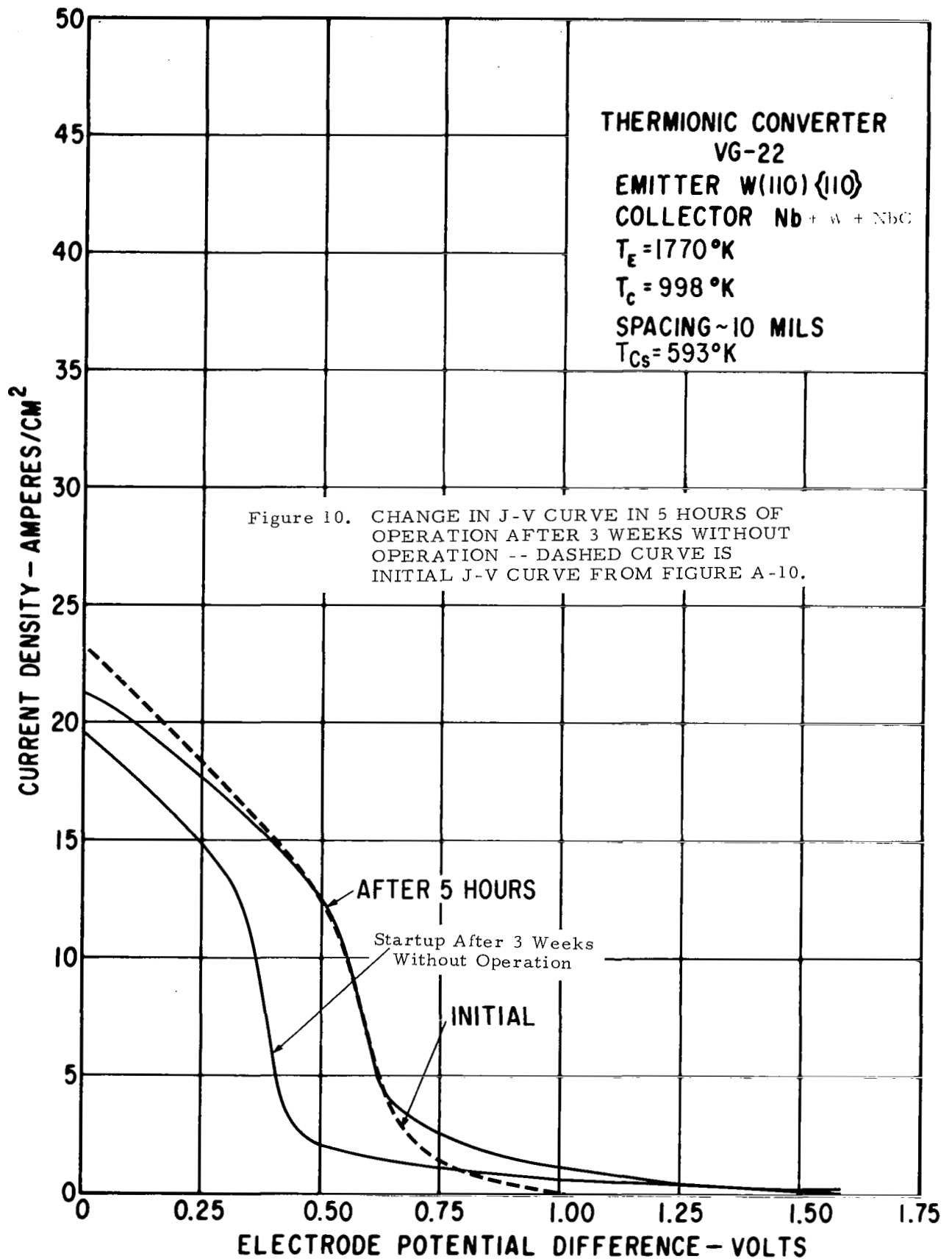


Figure 9. COLLECTOR WORK FUNCTION AFTER TAKING J-V CURVES (T_C/T_{Cs} VALUES ARE SUSPECT -- SEE PAGES 6 AND 7)



LIST OF SYMBOLS AND DEFINITIONS

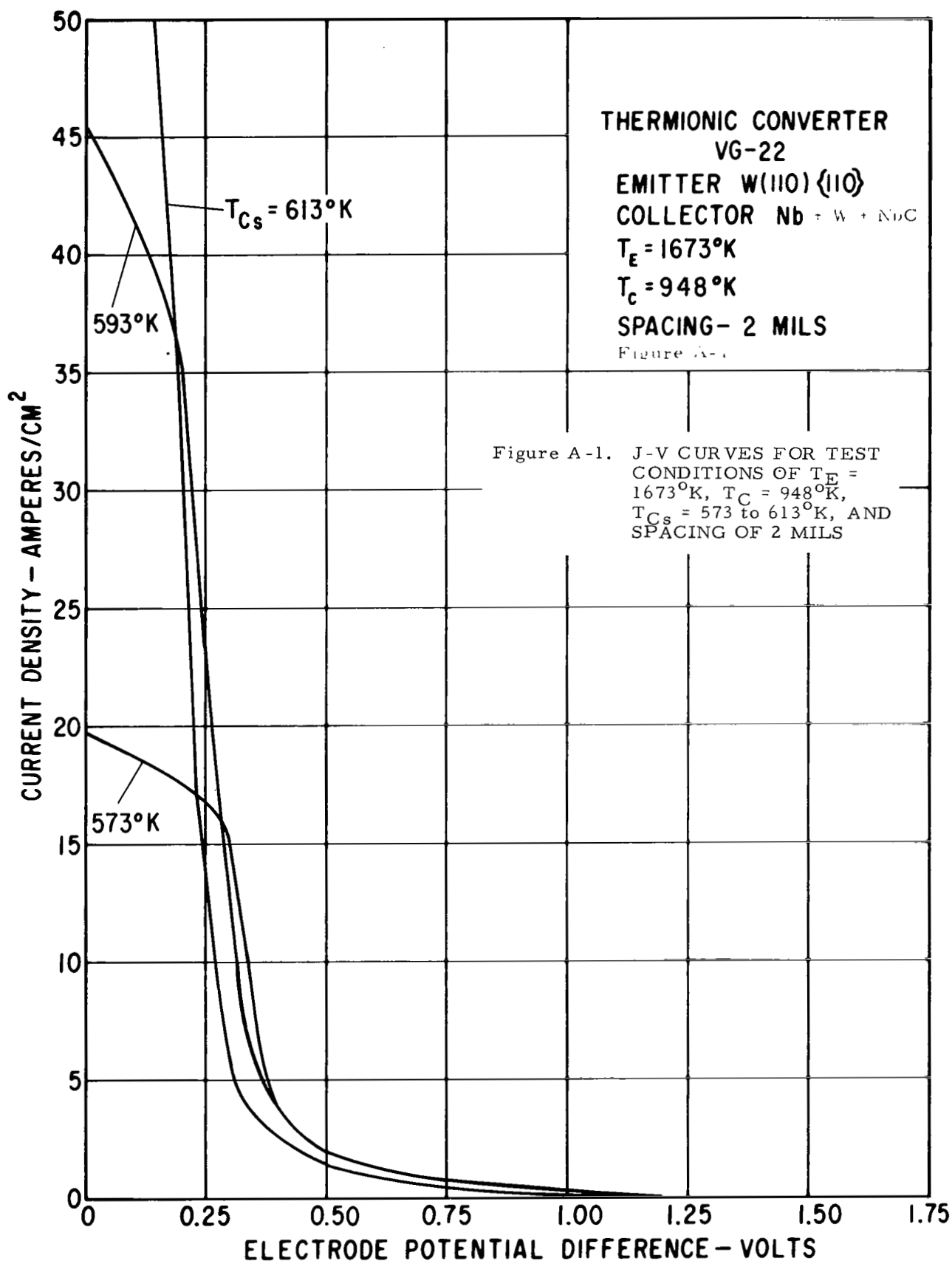
<u>SYMBOL</u>	<u>DEFINITION</u>
ϕ	Work Function -- Electron Volts
ϕ_E	Work Function of Emitter
ϕ_C	Work Function of Collector
eV	Electron Volts
T_E	Temperature of the Emitter
T_C	Temperature of the Collector
T_{Cs}	Temperature of the Cesium Reservoir
J-V	Current Density Versus Voltage Curves

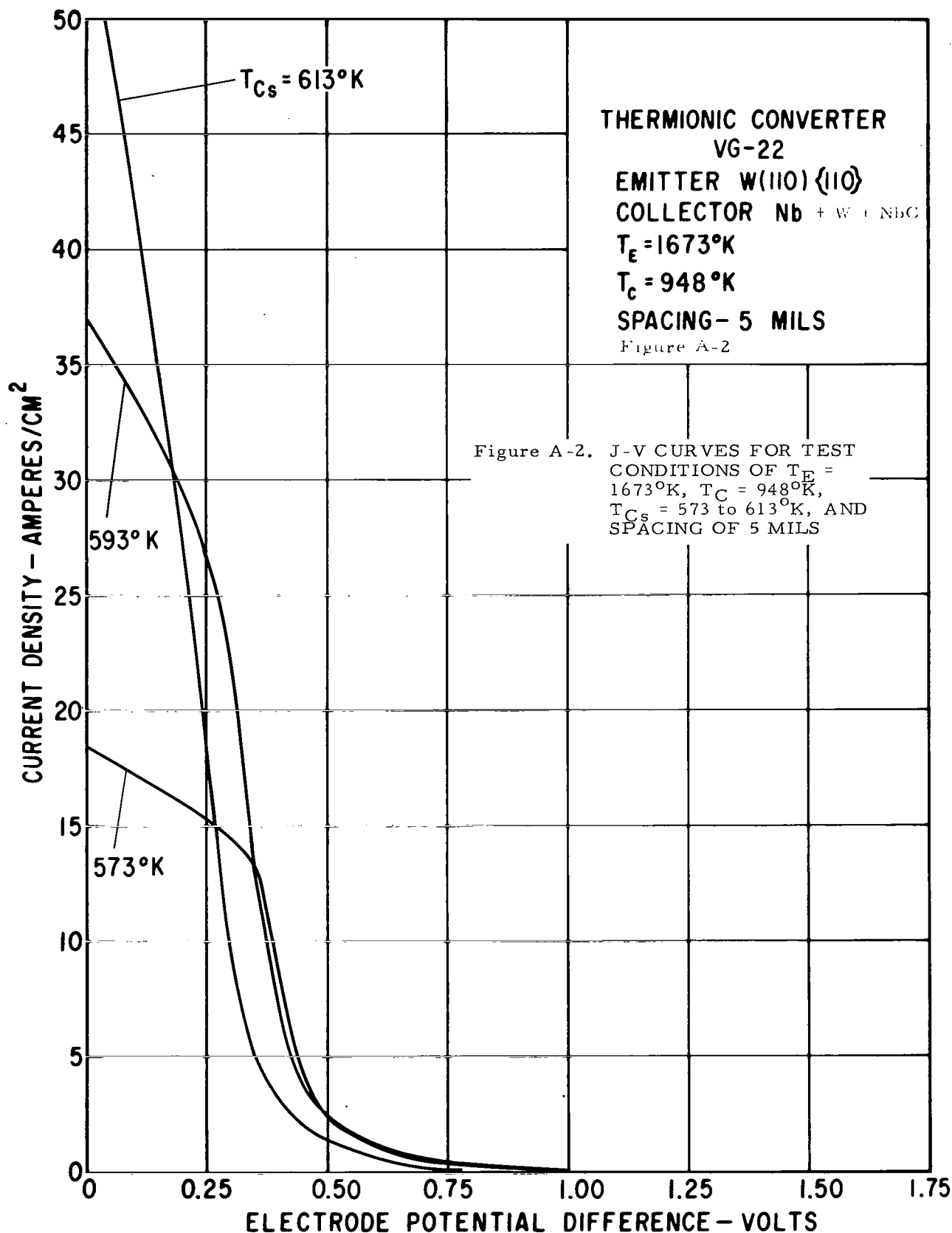
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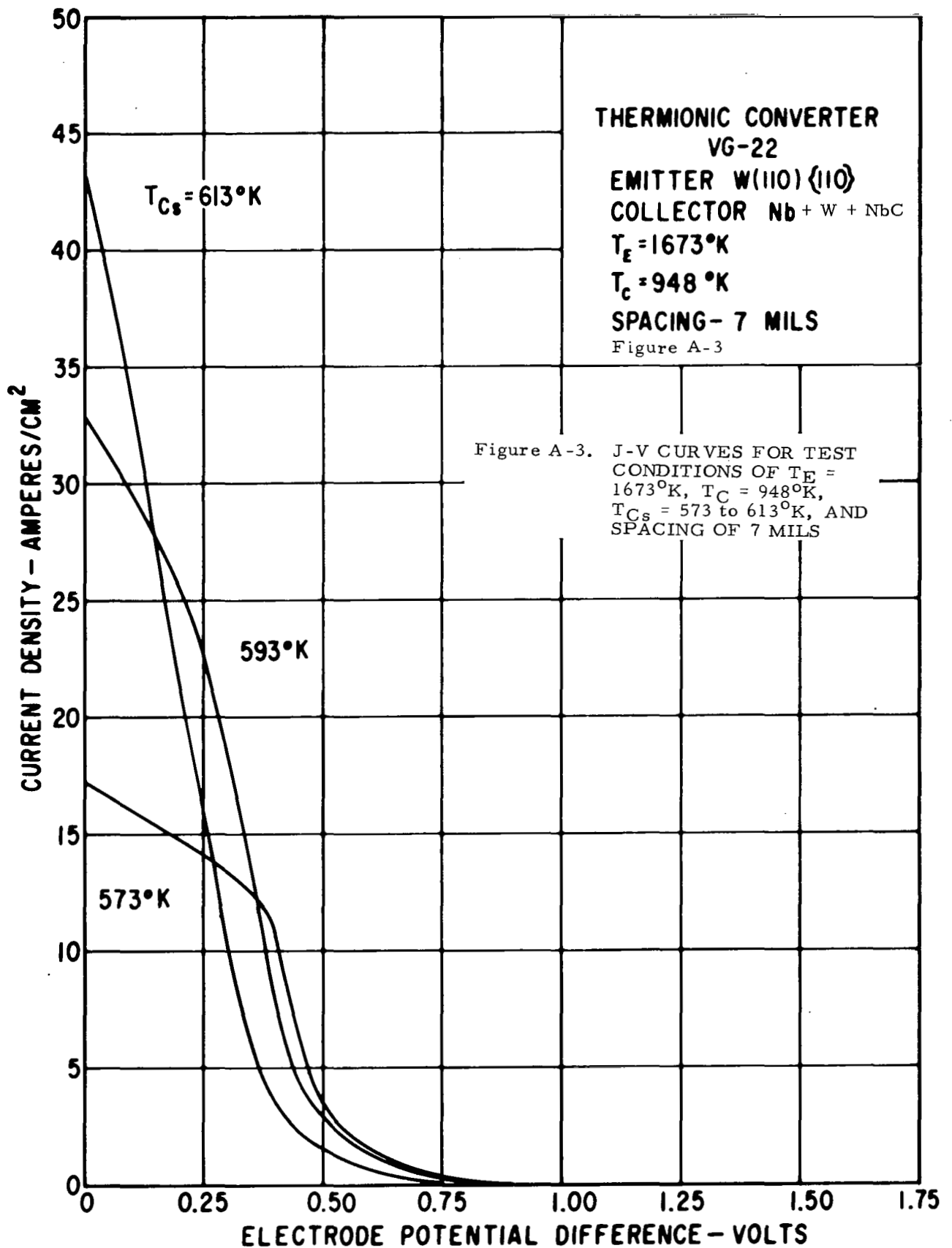
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- (6) Ibid., Figure 5.
- (7) Lawrence, J. and Wilson, V. C., Therm. Conf. Specialist Conf., p. 6 (1966).
- (8) Wilson, V. C. and Lawrence, J., "Characteristics of a Variable Spaced Planar Thermionic Converter with a Tungsten Emitter and a Niobium Collector," NASA CR-1033, 1968.
- (9) Wilson, V. C. and Lawrence, J., Therm. Conv. Specialist Conf., p. 1 (1967); also "Characteristics of a Thermionic Converter with a Fluoride Vapor Deposited Tungsten Emitter Etched to Preferentially Expose the 110 Crystal Planes," NASA CR-1381, (1969).
- (10) Wilson, V. C. and Podkulski, S. P., "Characteristics of a Thermionic Converter with a Chloride Vapor Deposited Tungsten Emitter (110) and a Nickel Collector," NASA CR-1416, 1970.

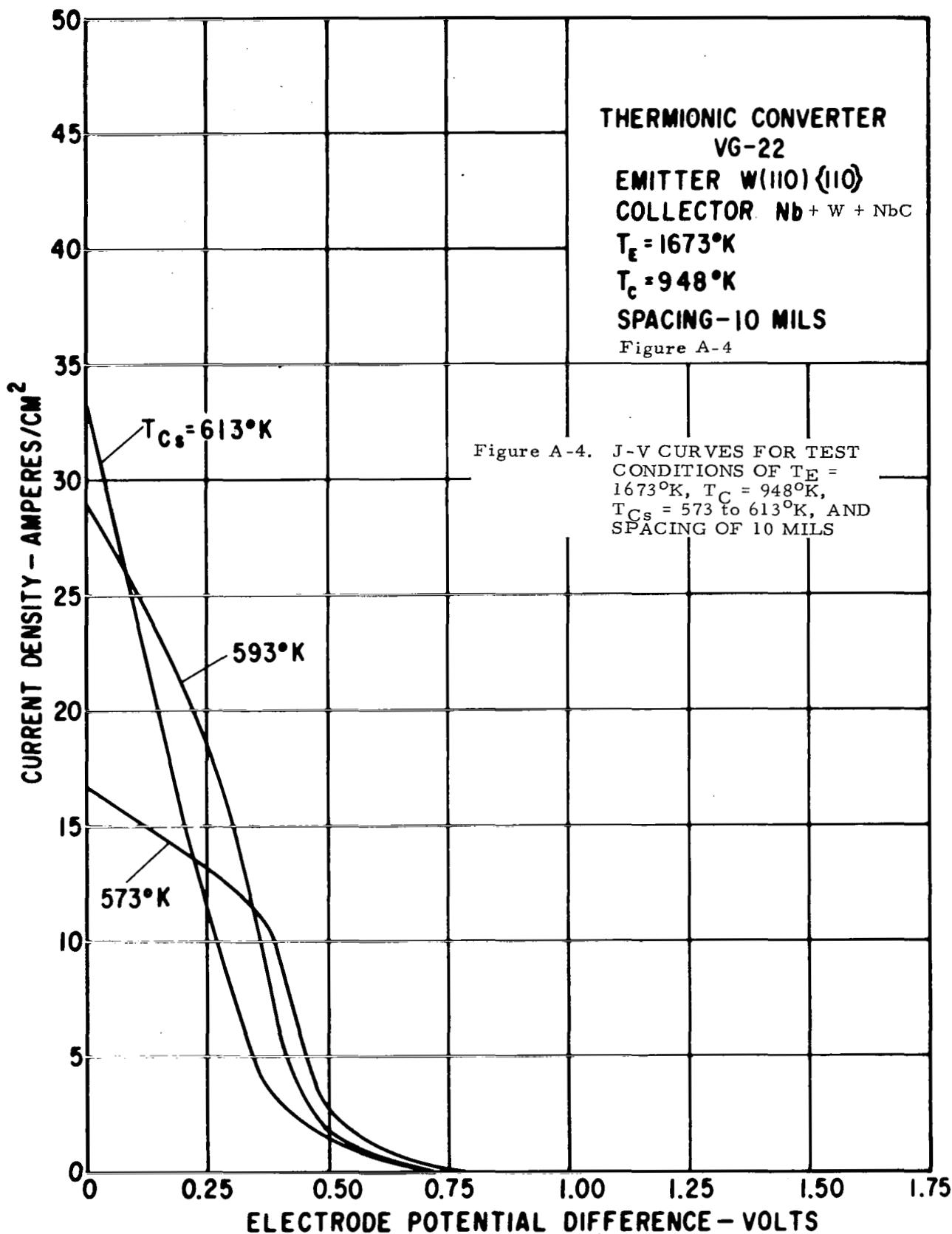
APPENDIX A

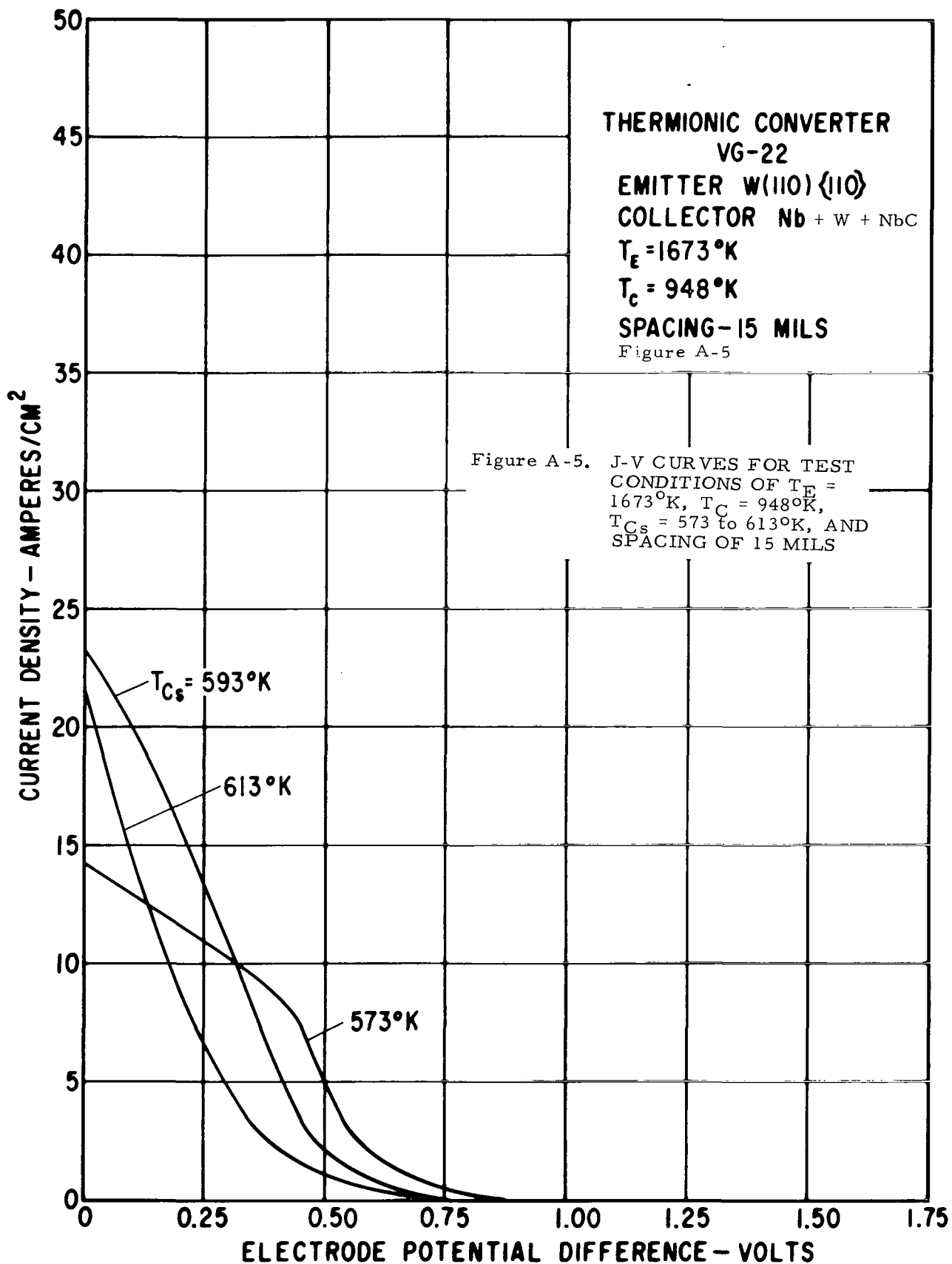
The current density versus voltage curves (J-V curves) are given here for a thermionic converter with a chloride vapor deposited tungsten emitter having the (110) oriented planes parallel to the bulk surface and with a polycrystalline niobium collector coated with a thin tungsten film and a trace of niobium carbide.

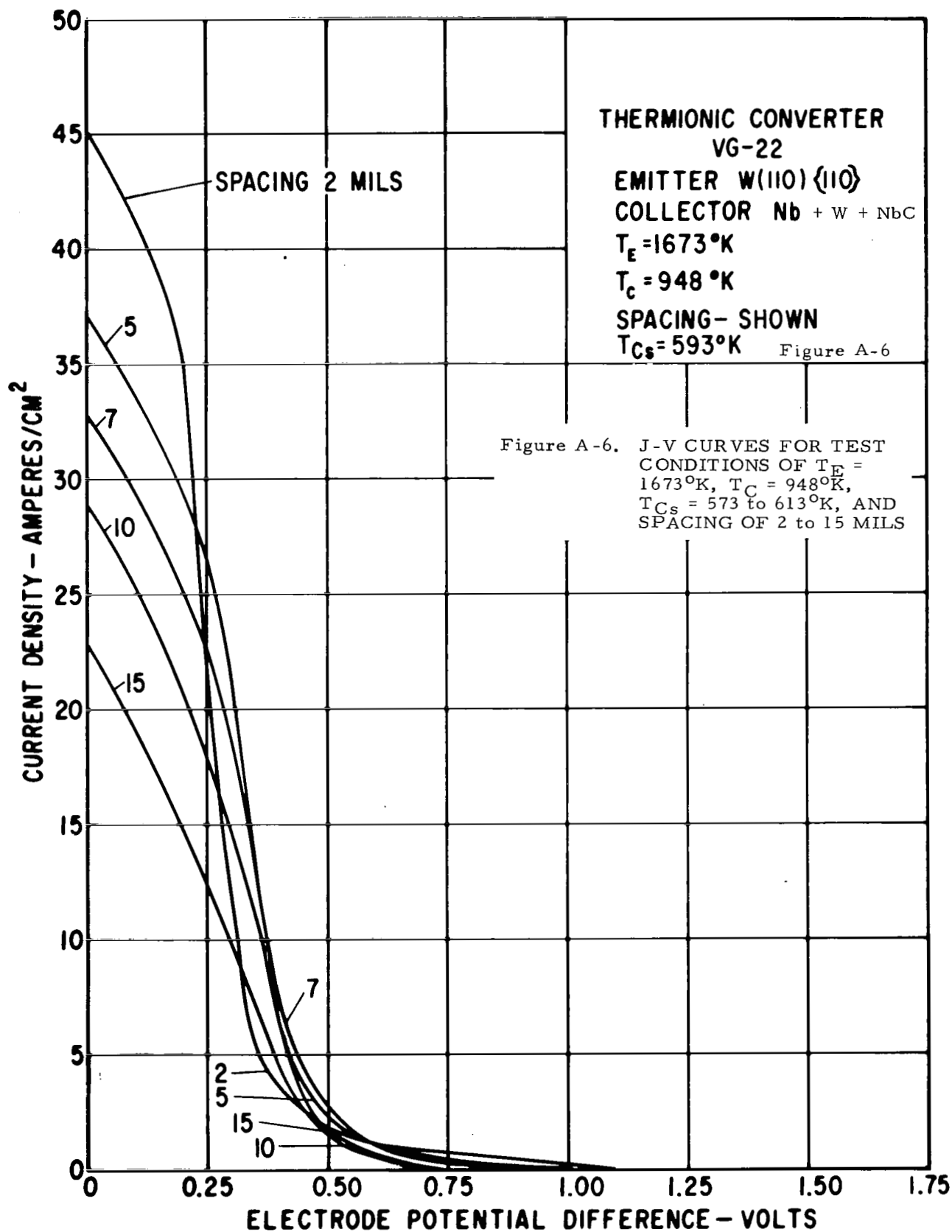


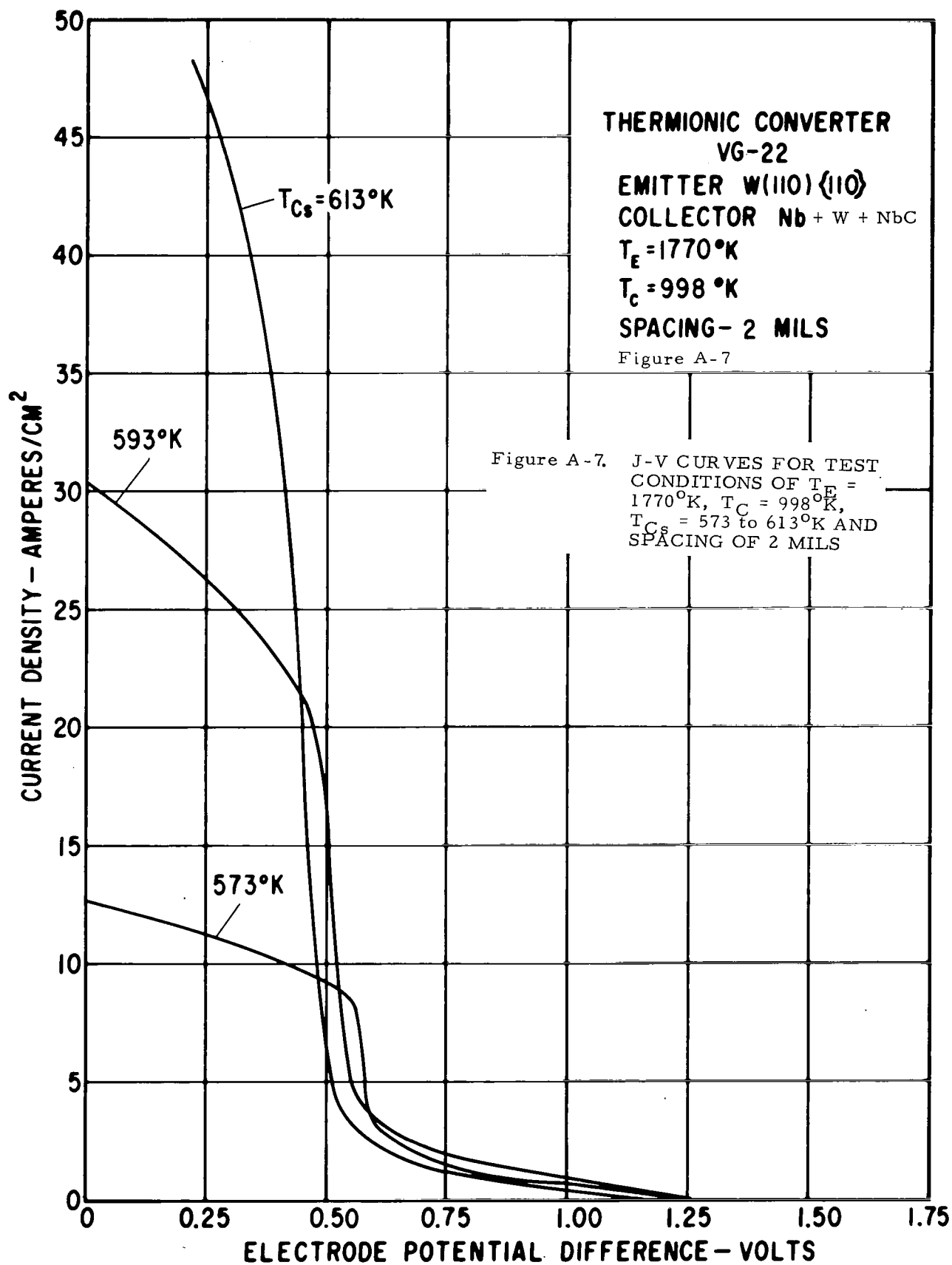


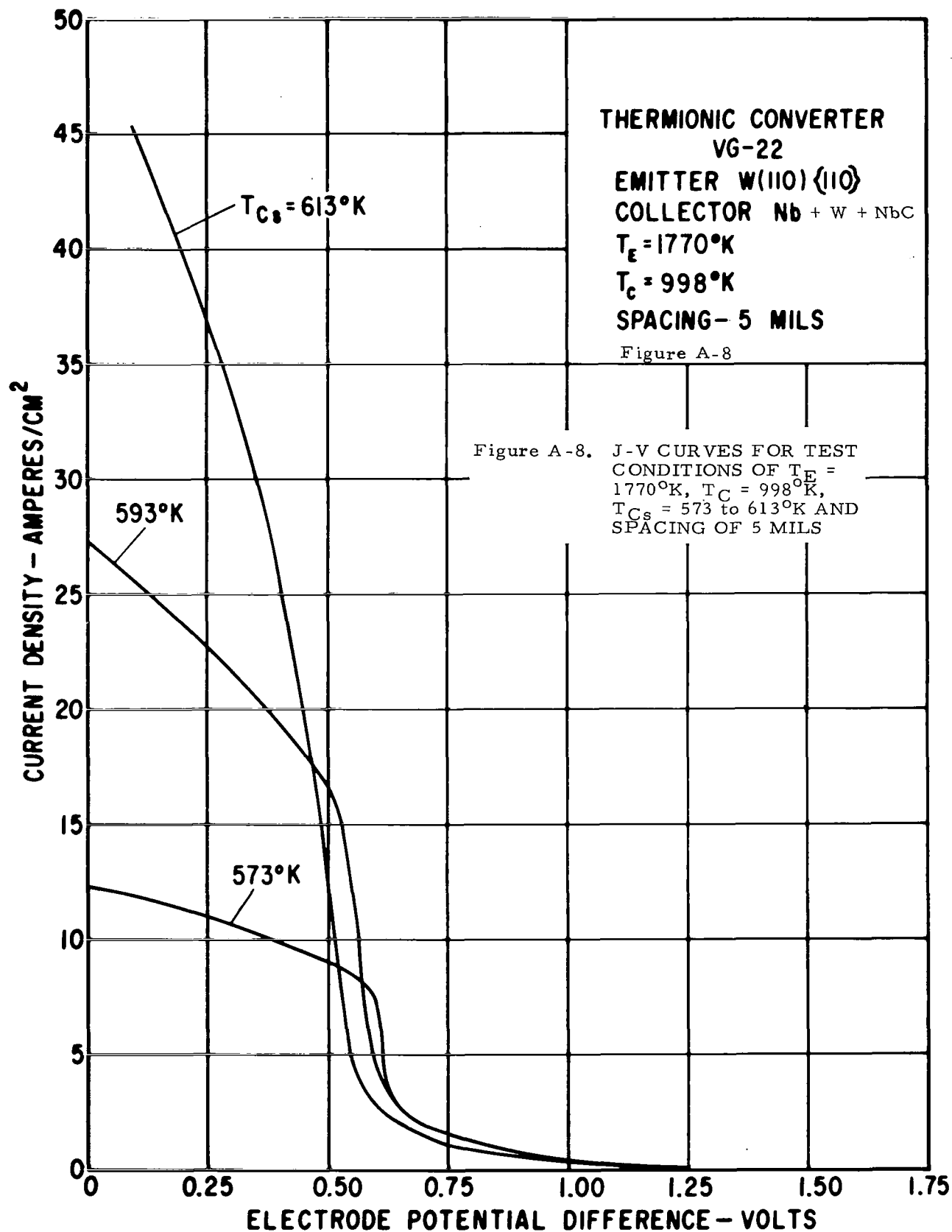


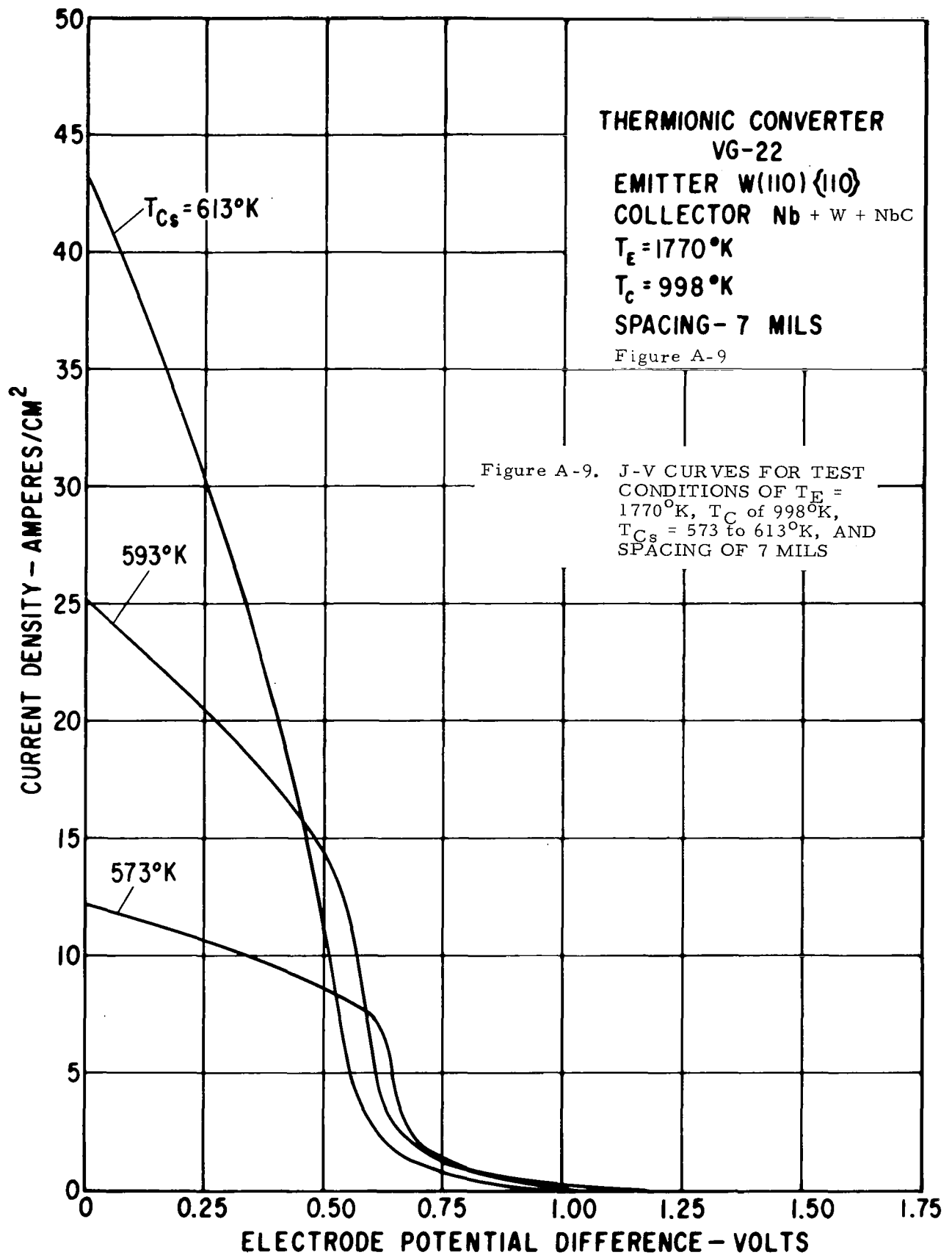


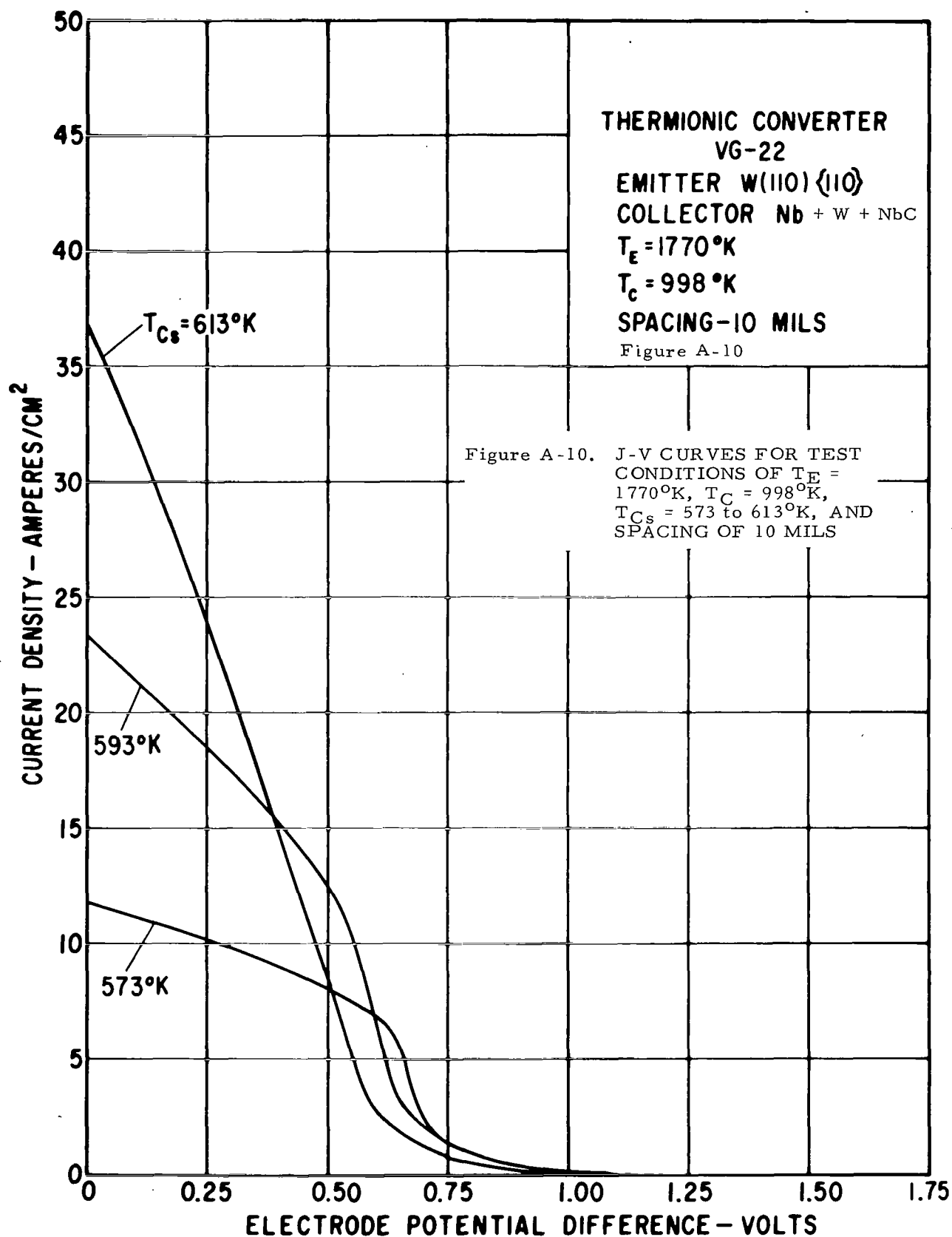


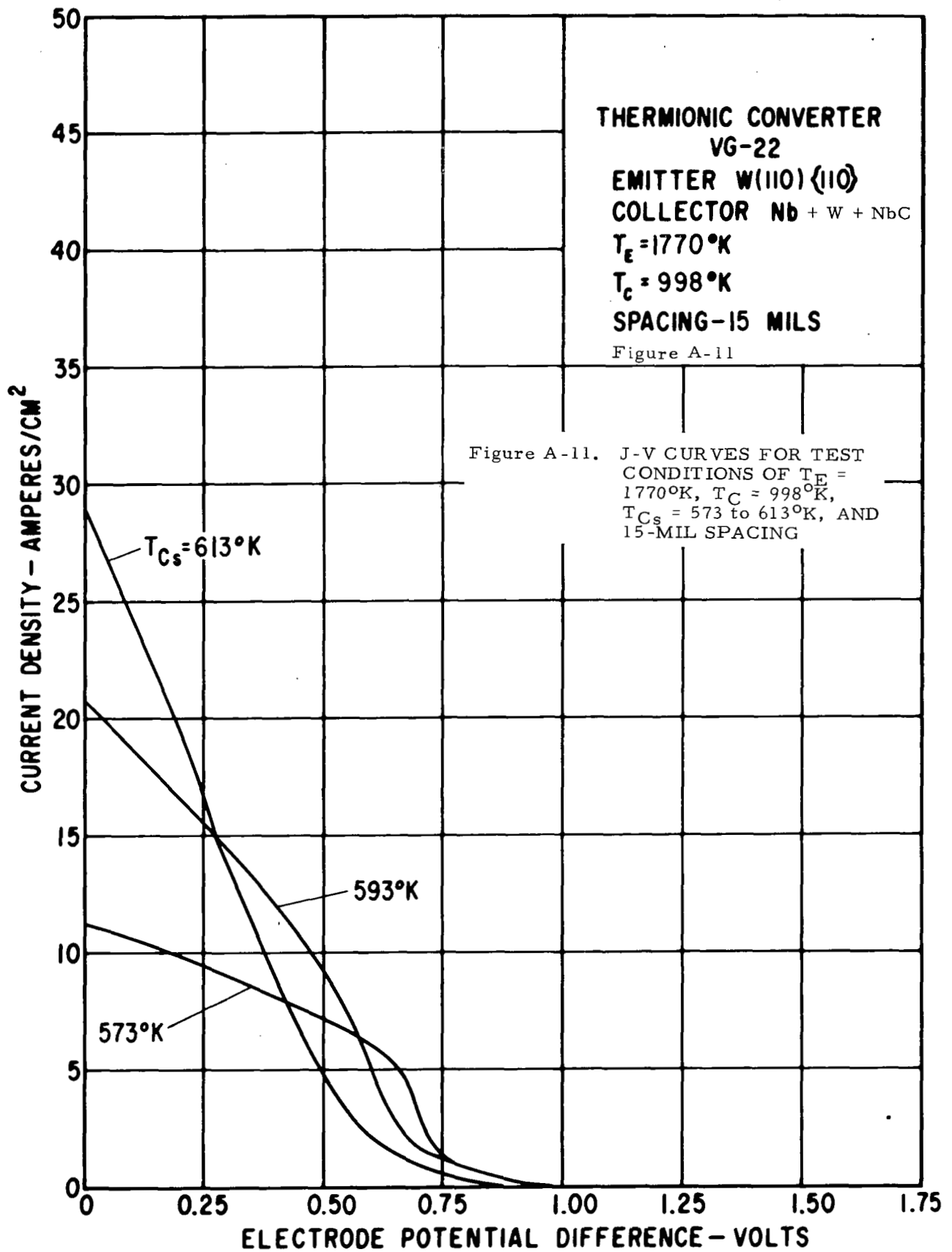


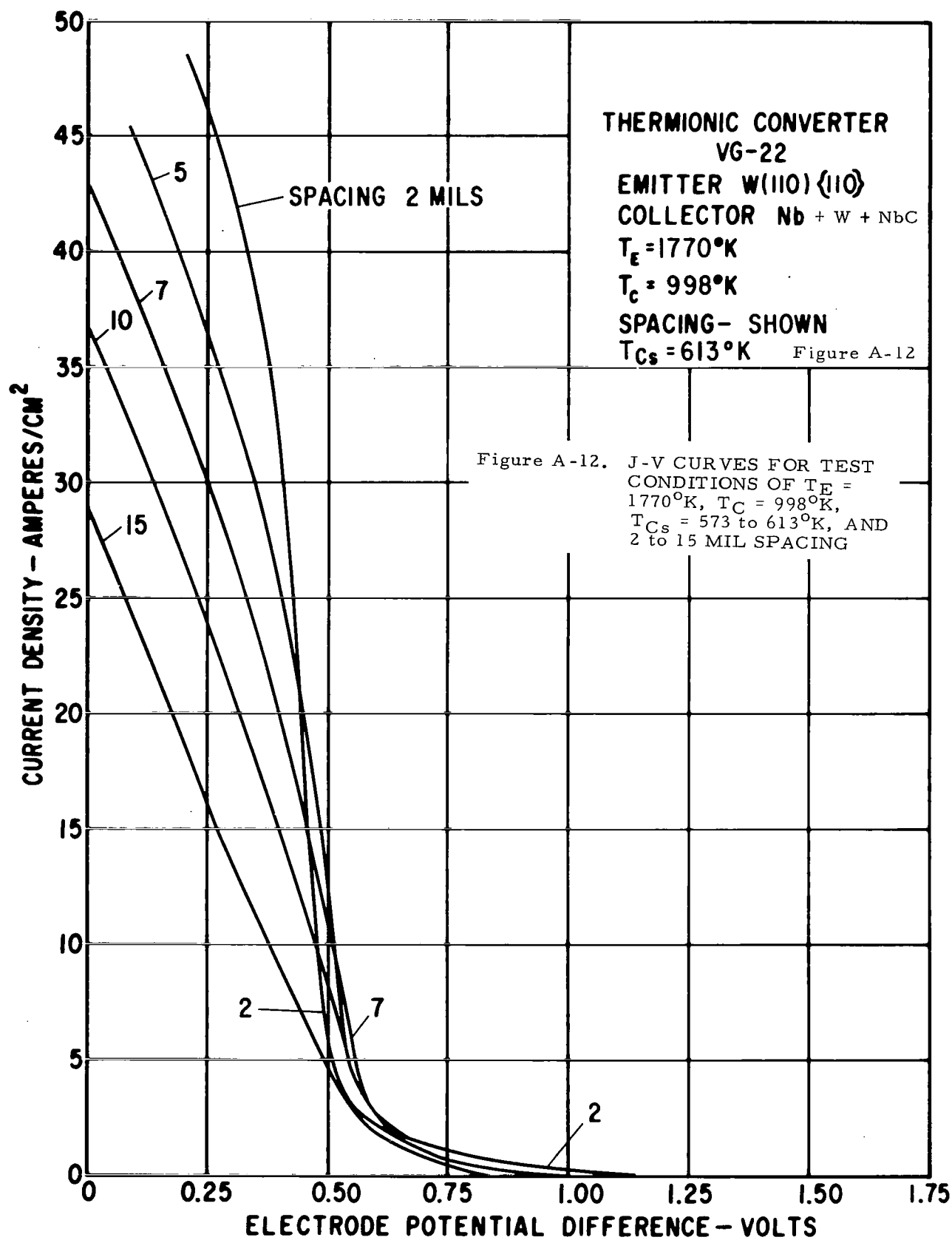


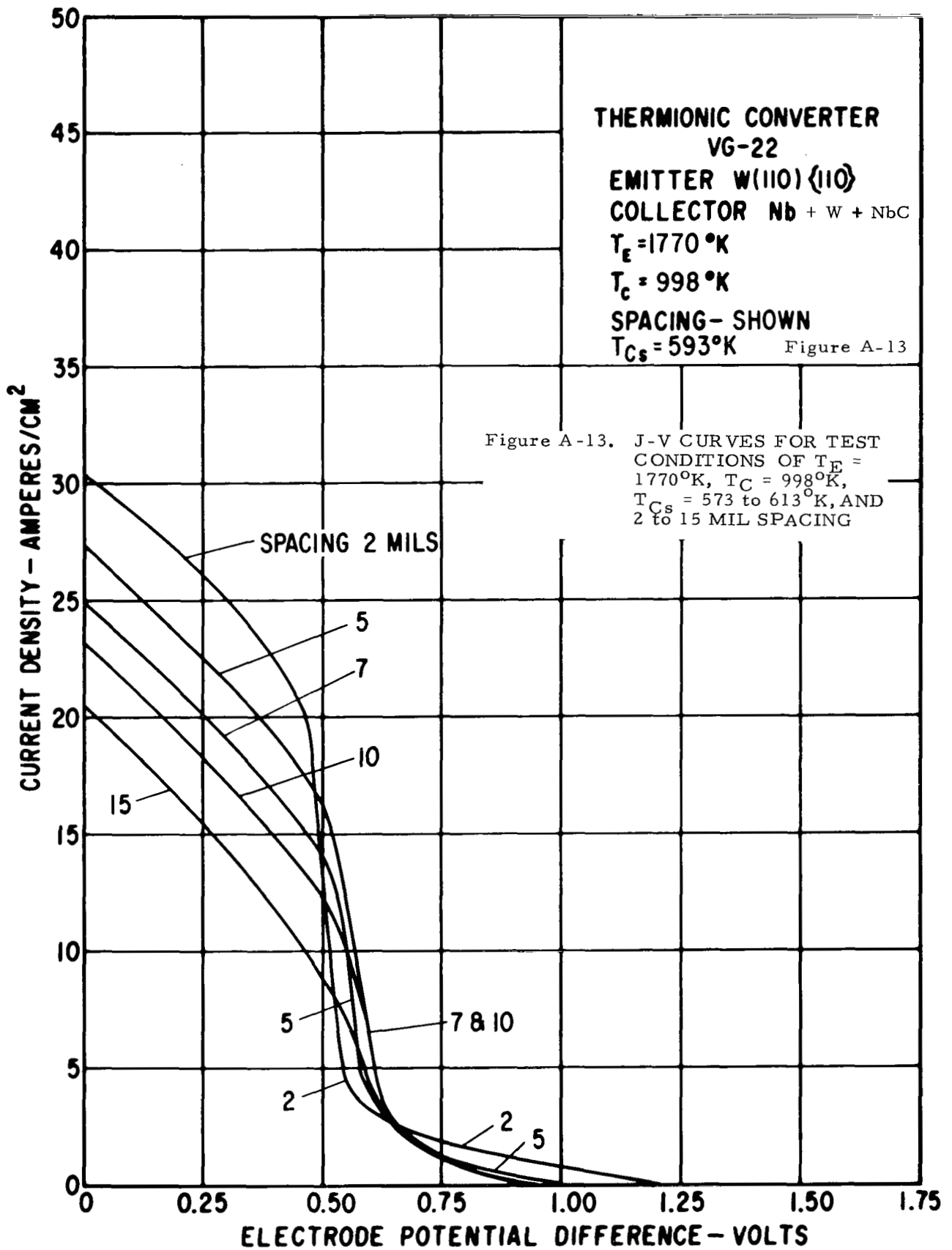


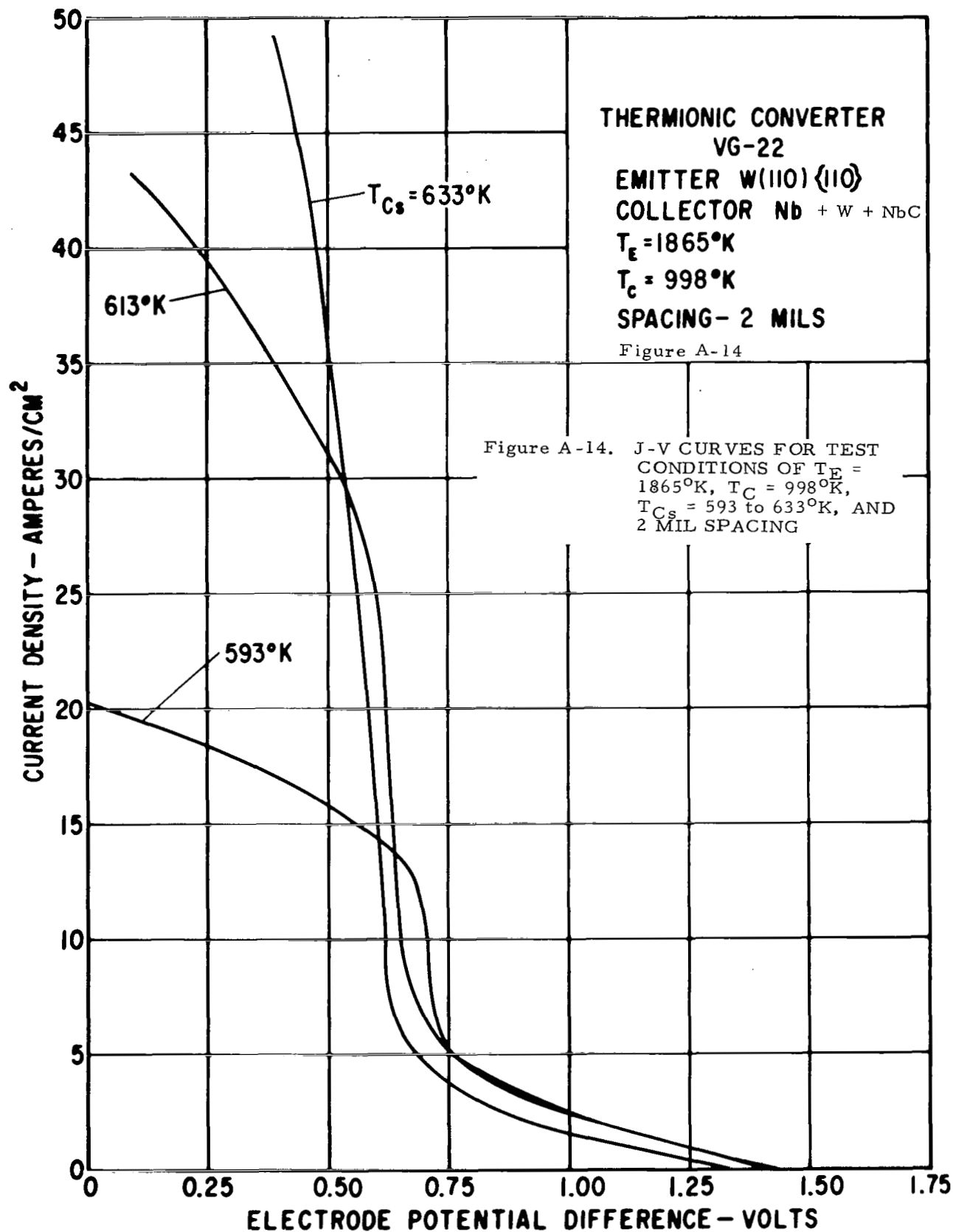


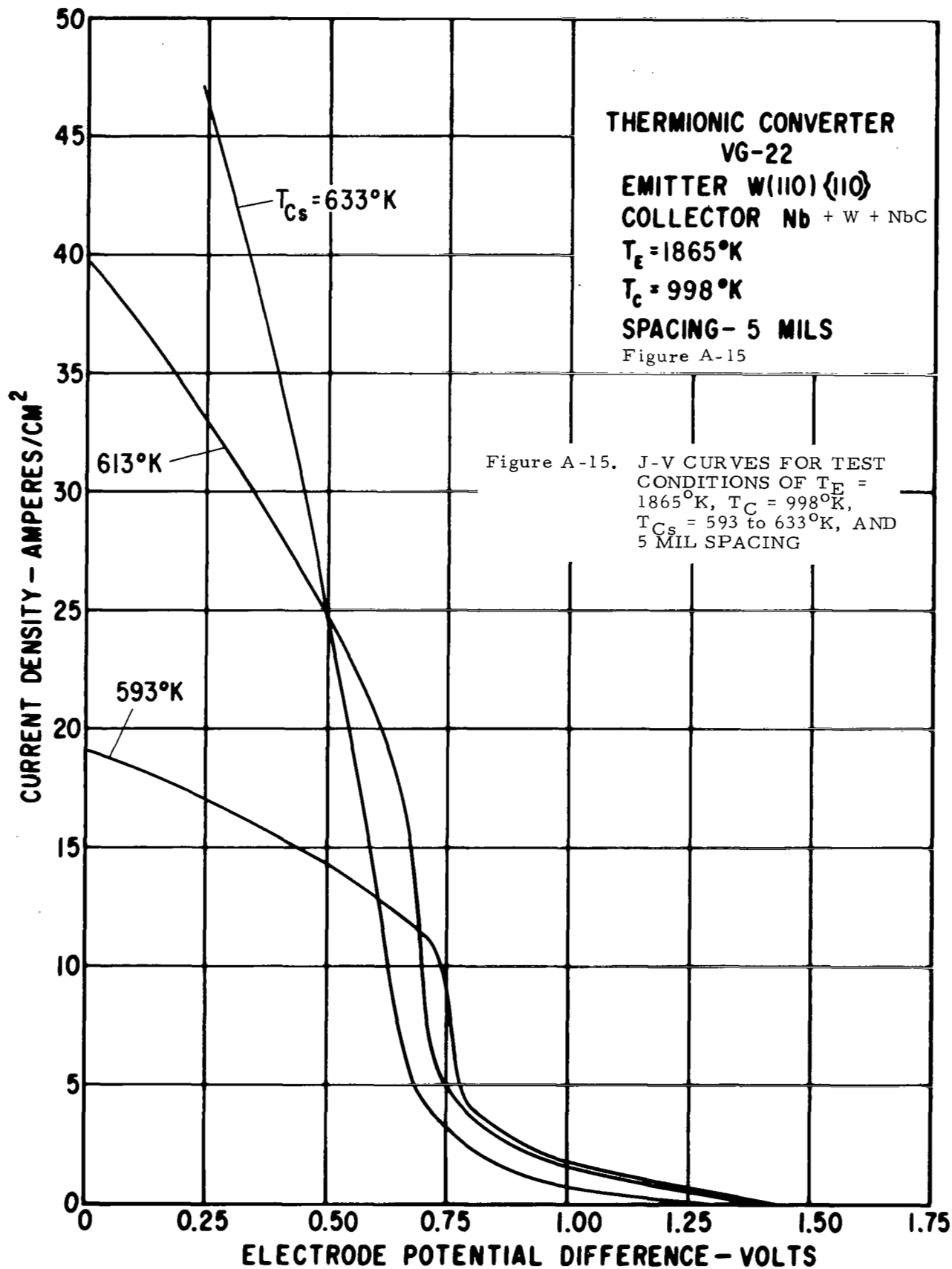


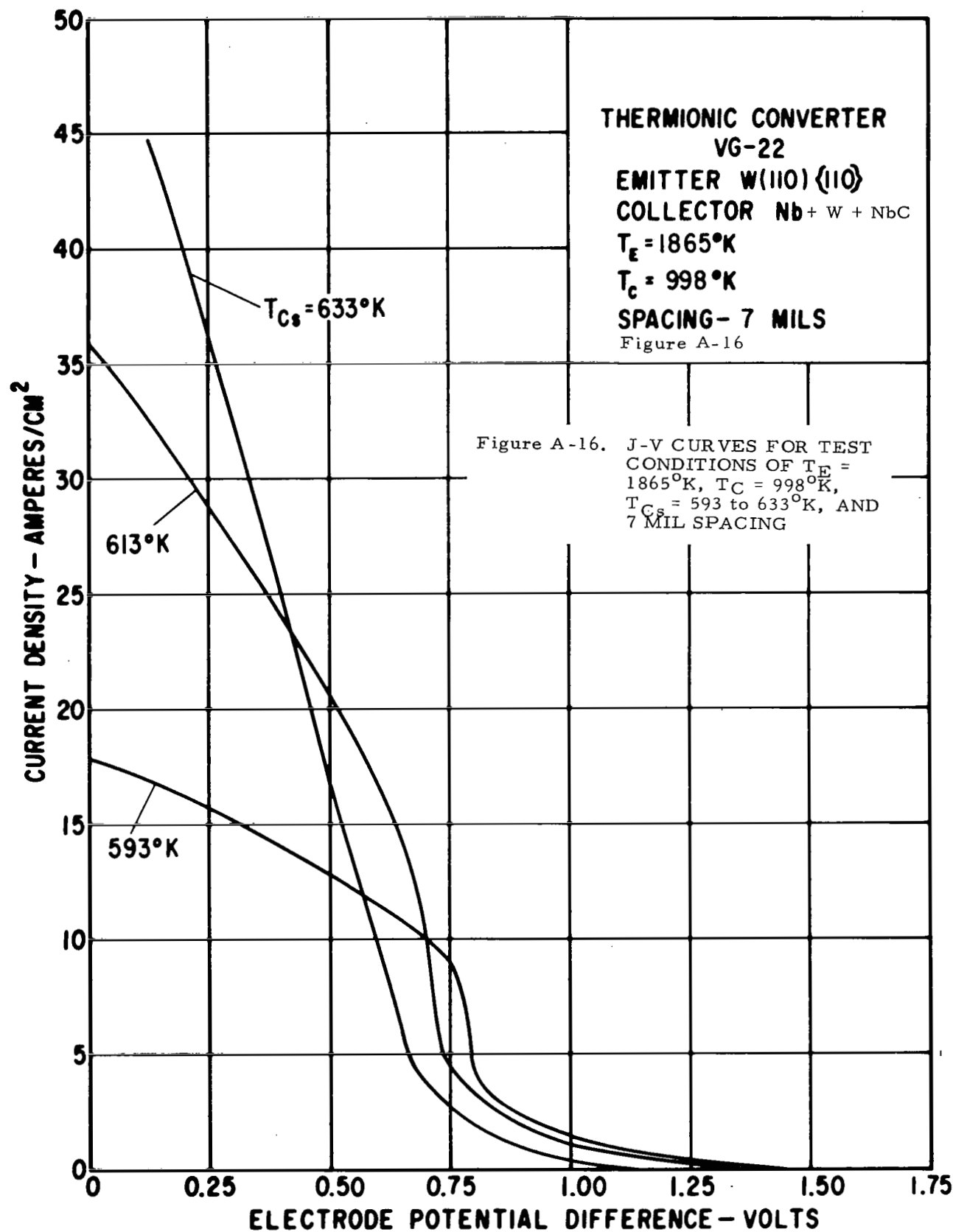


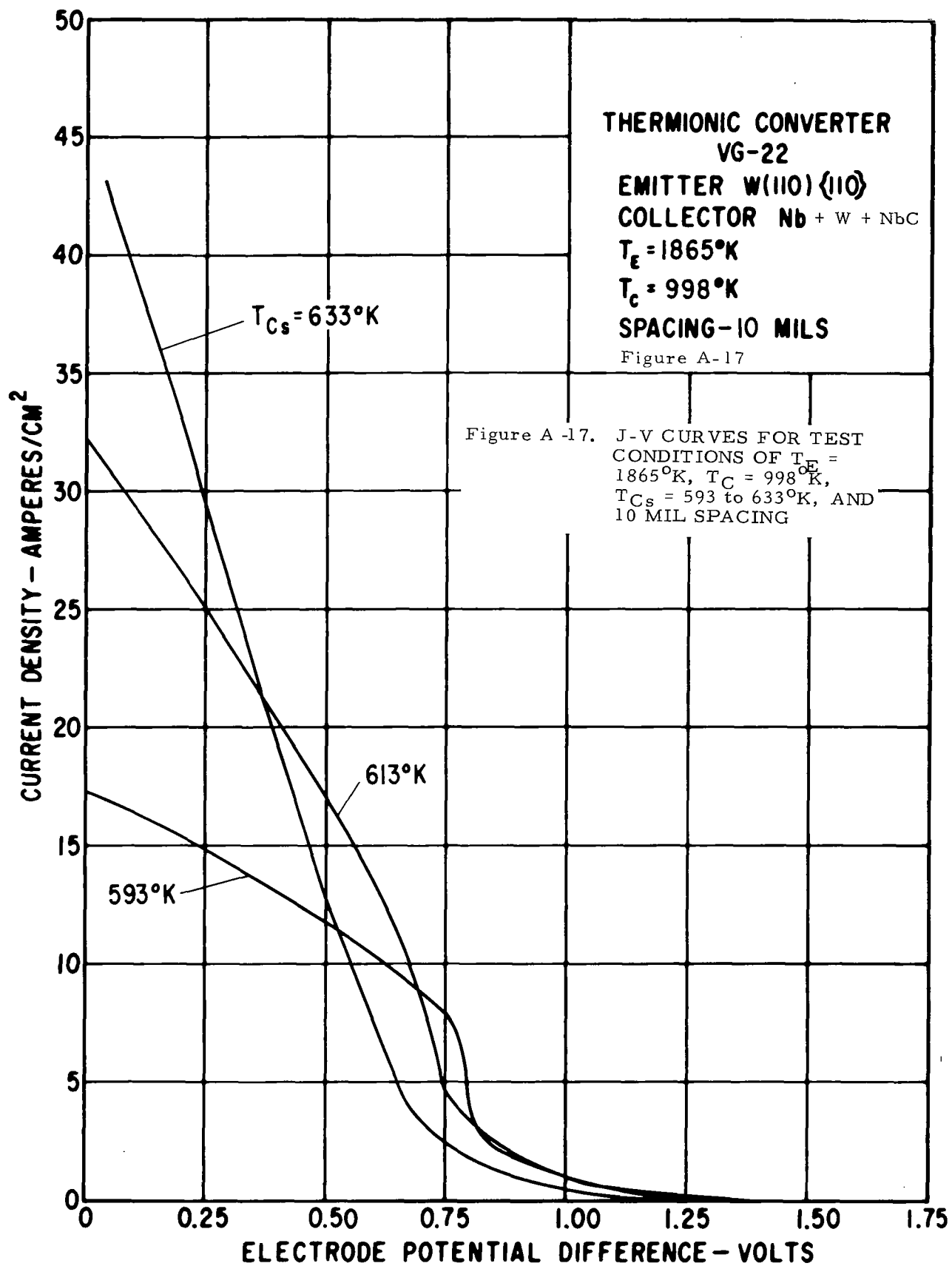


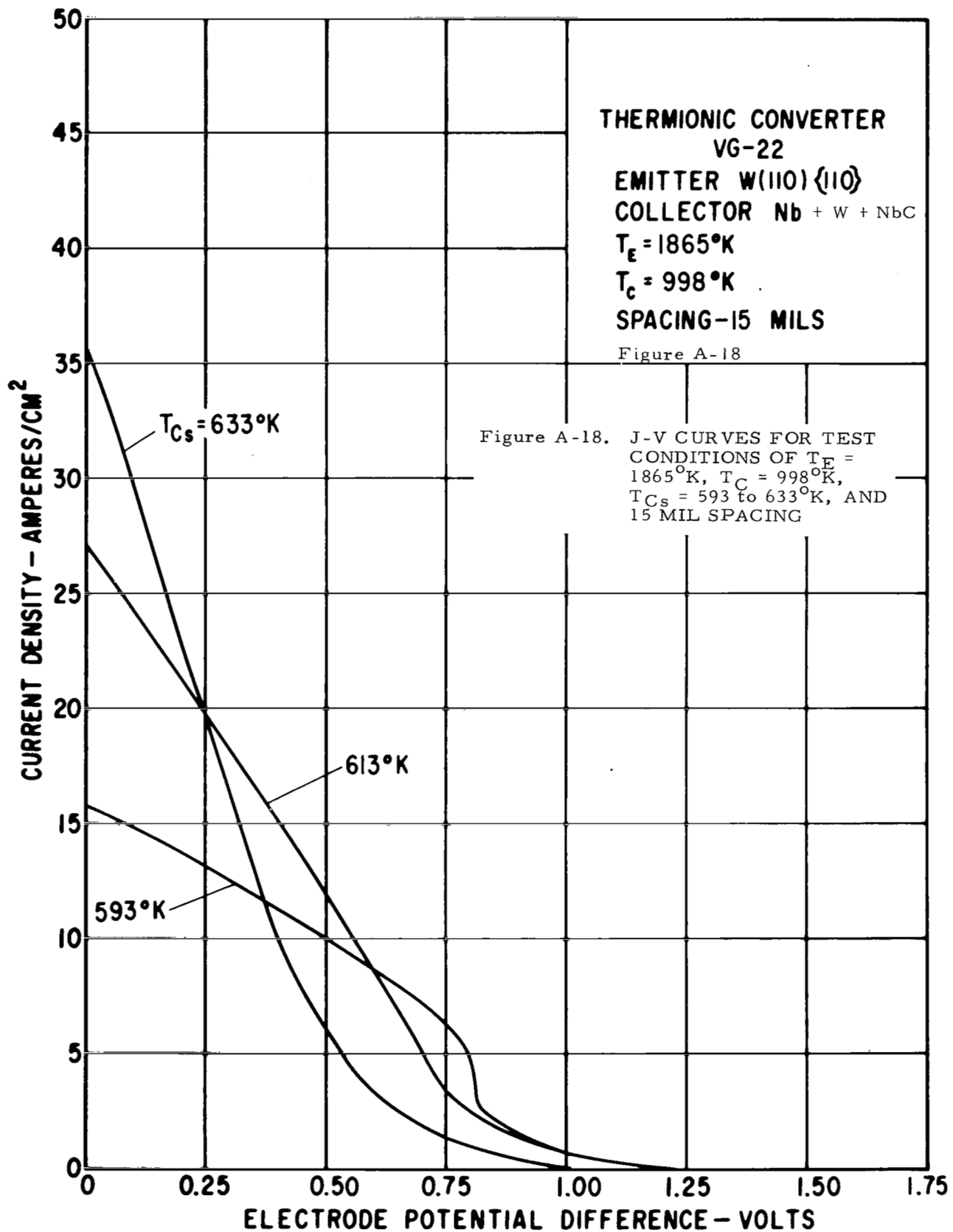


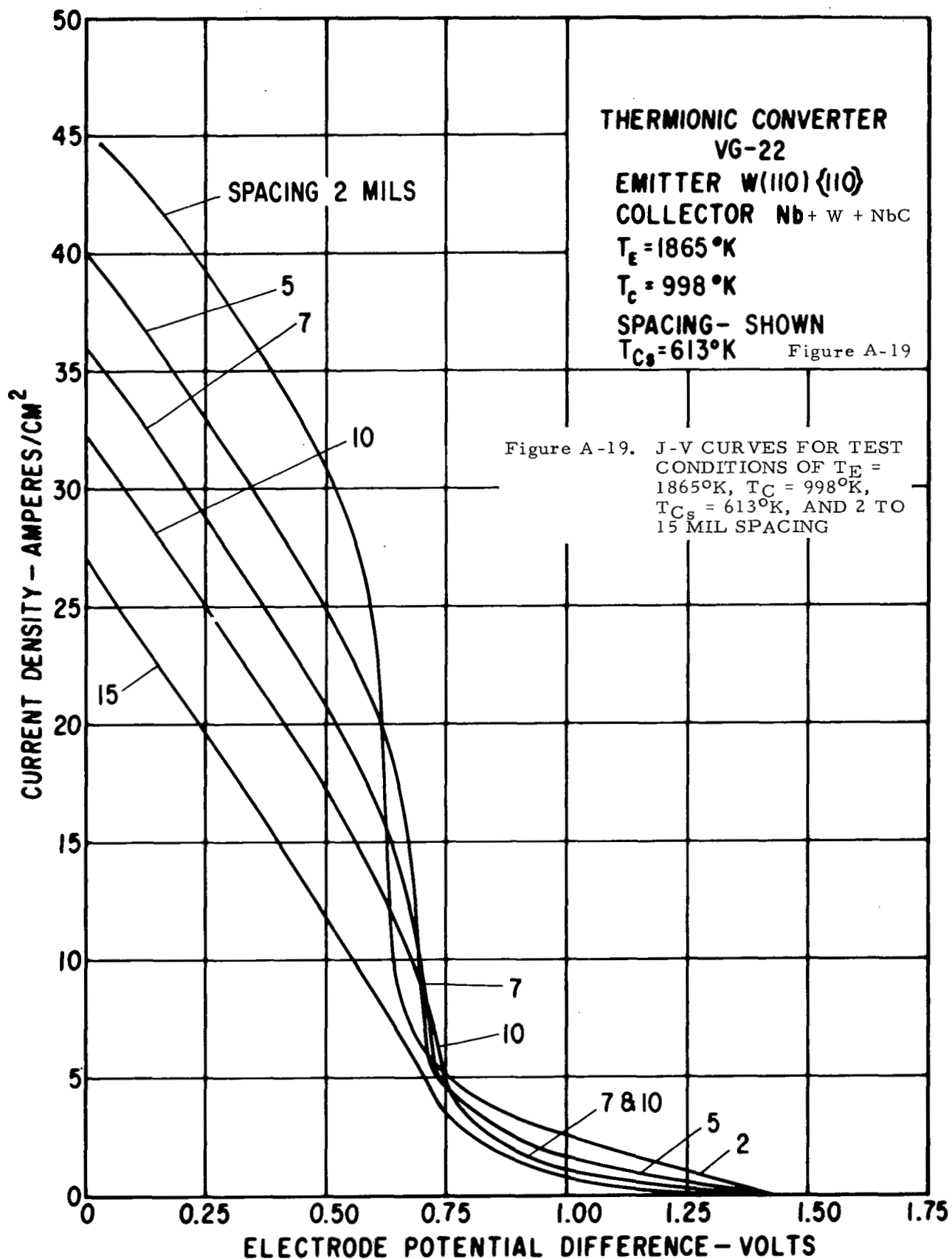


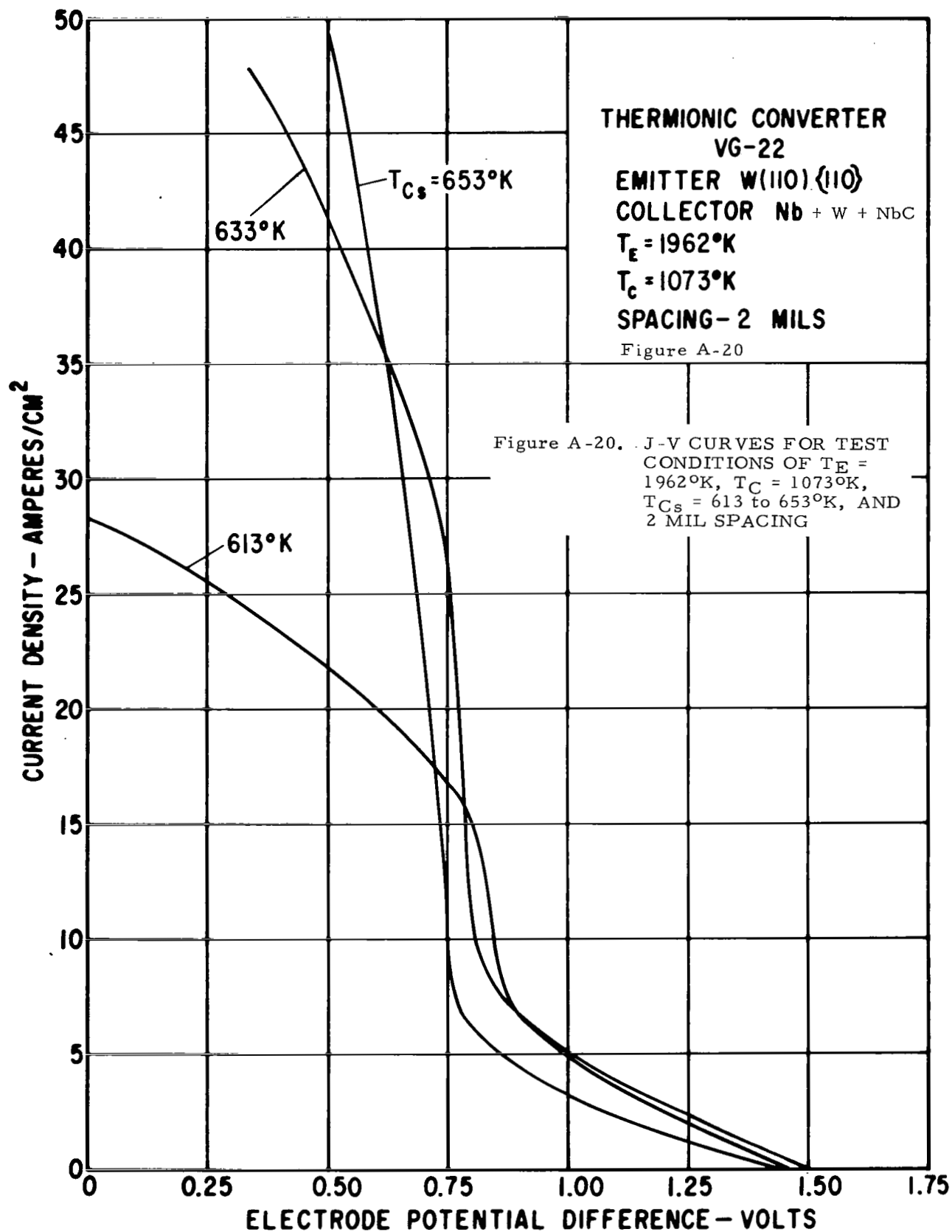


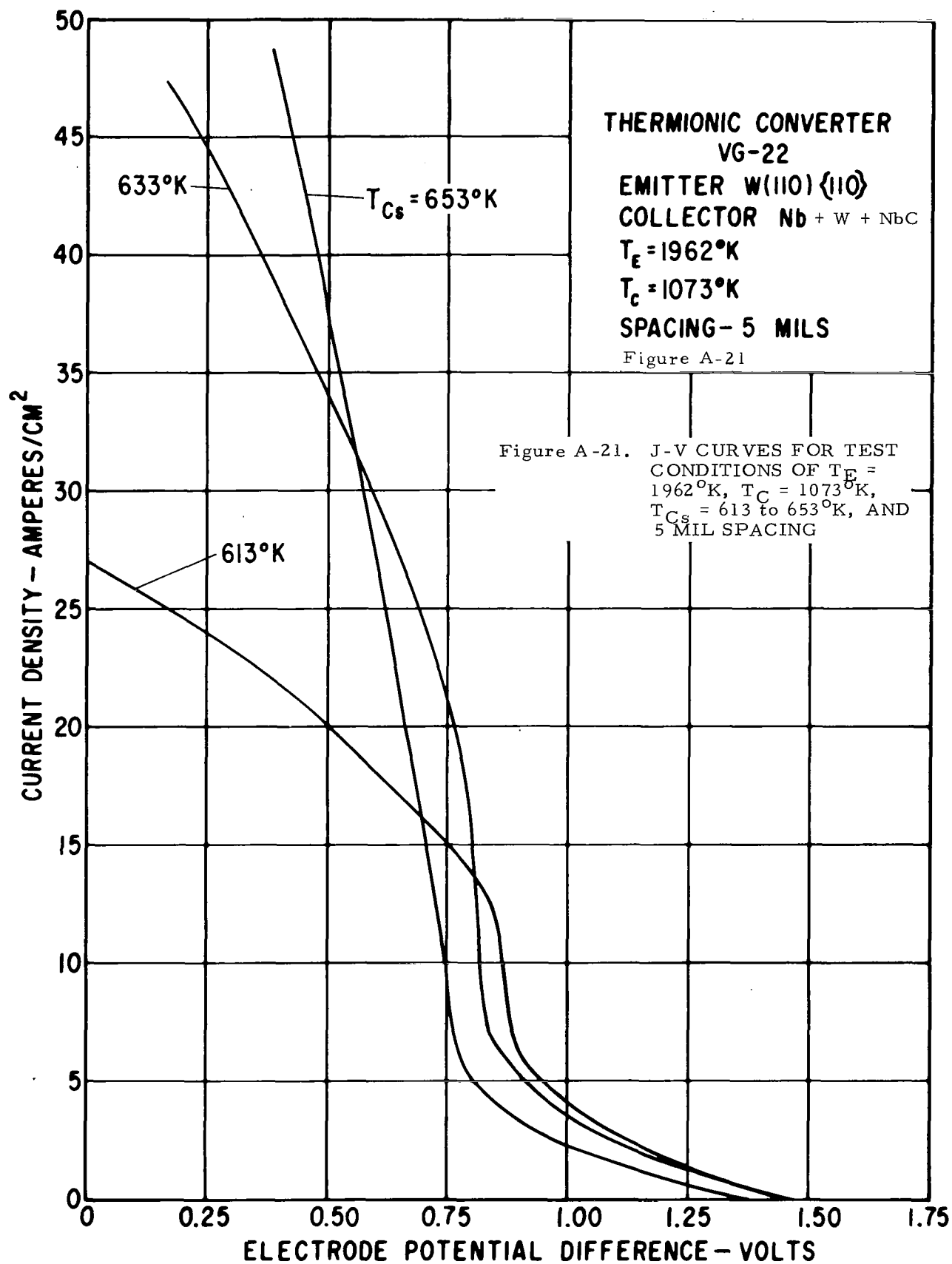


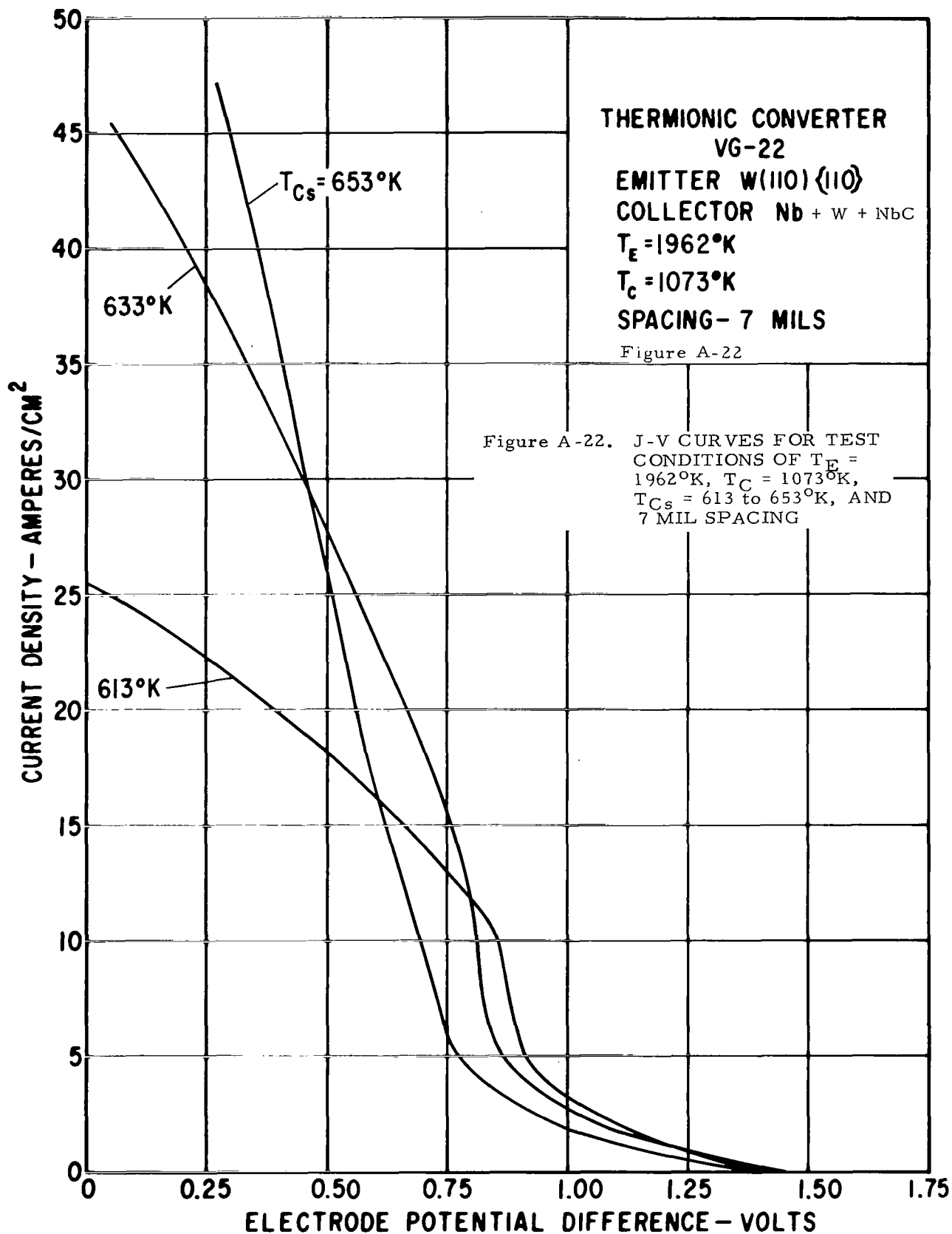


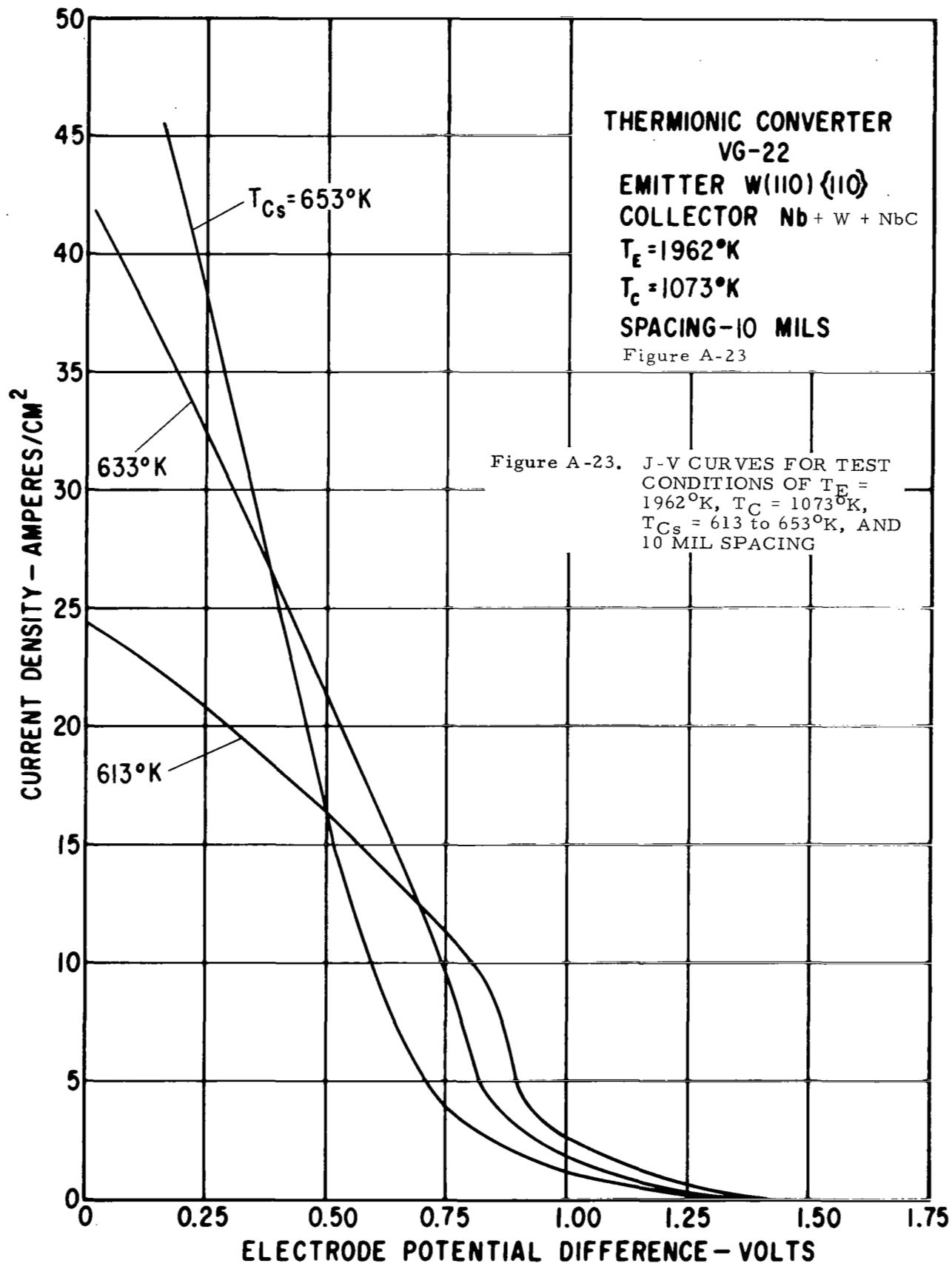


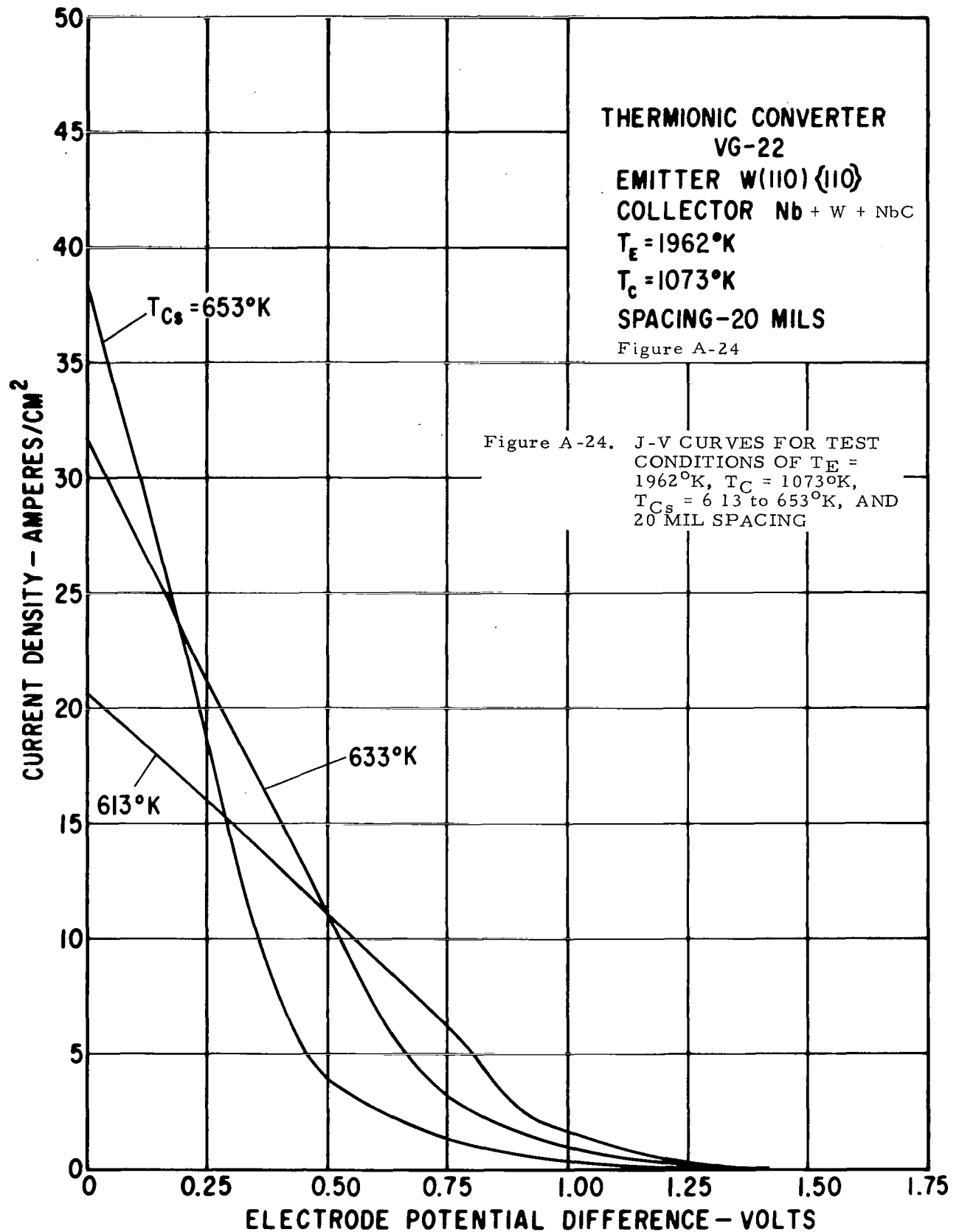


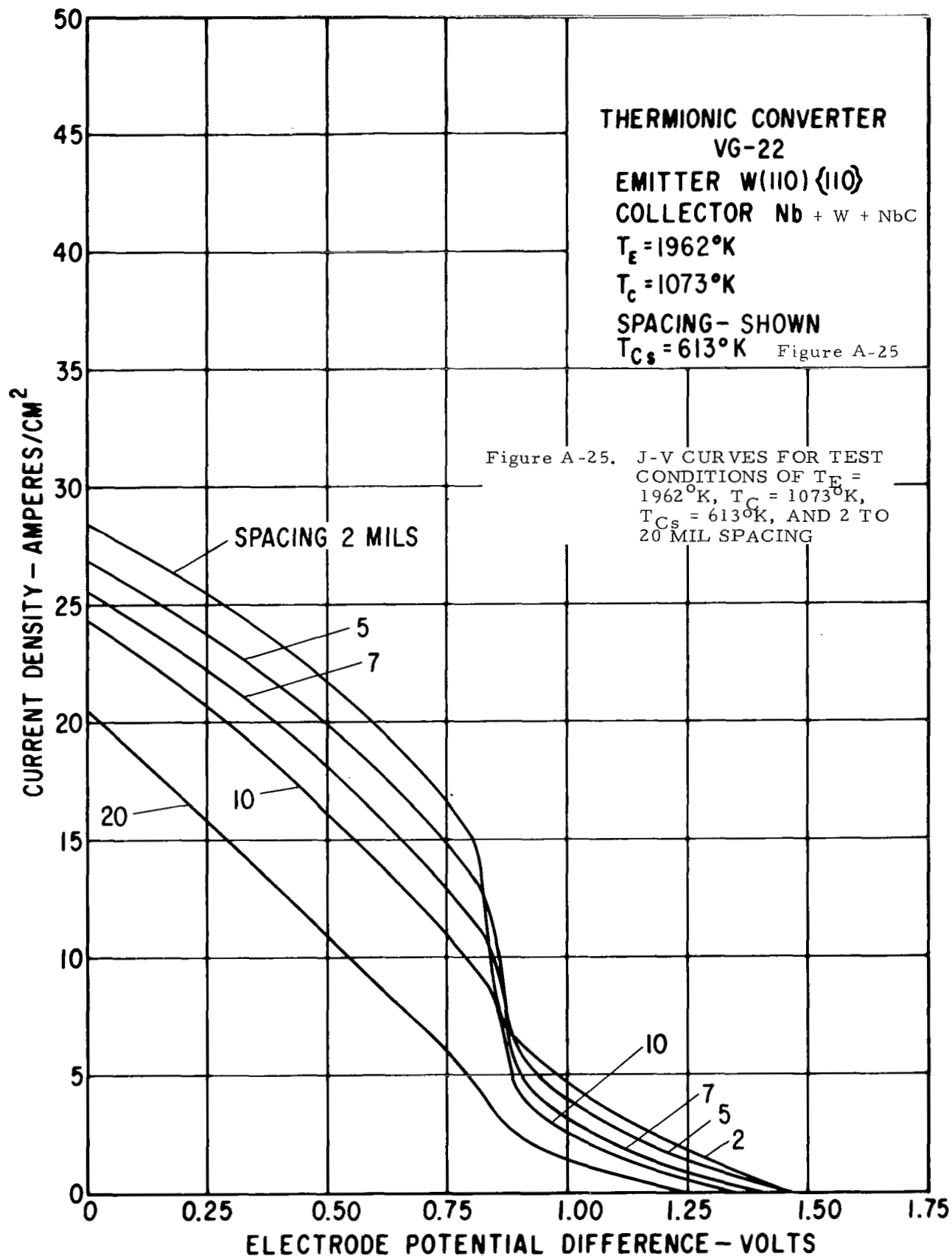


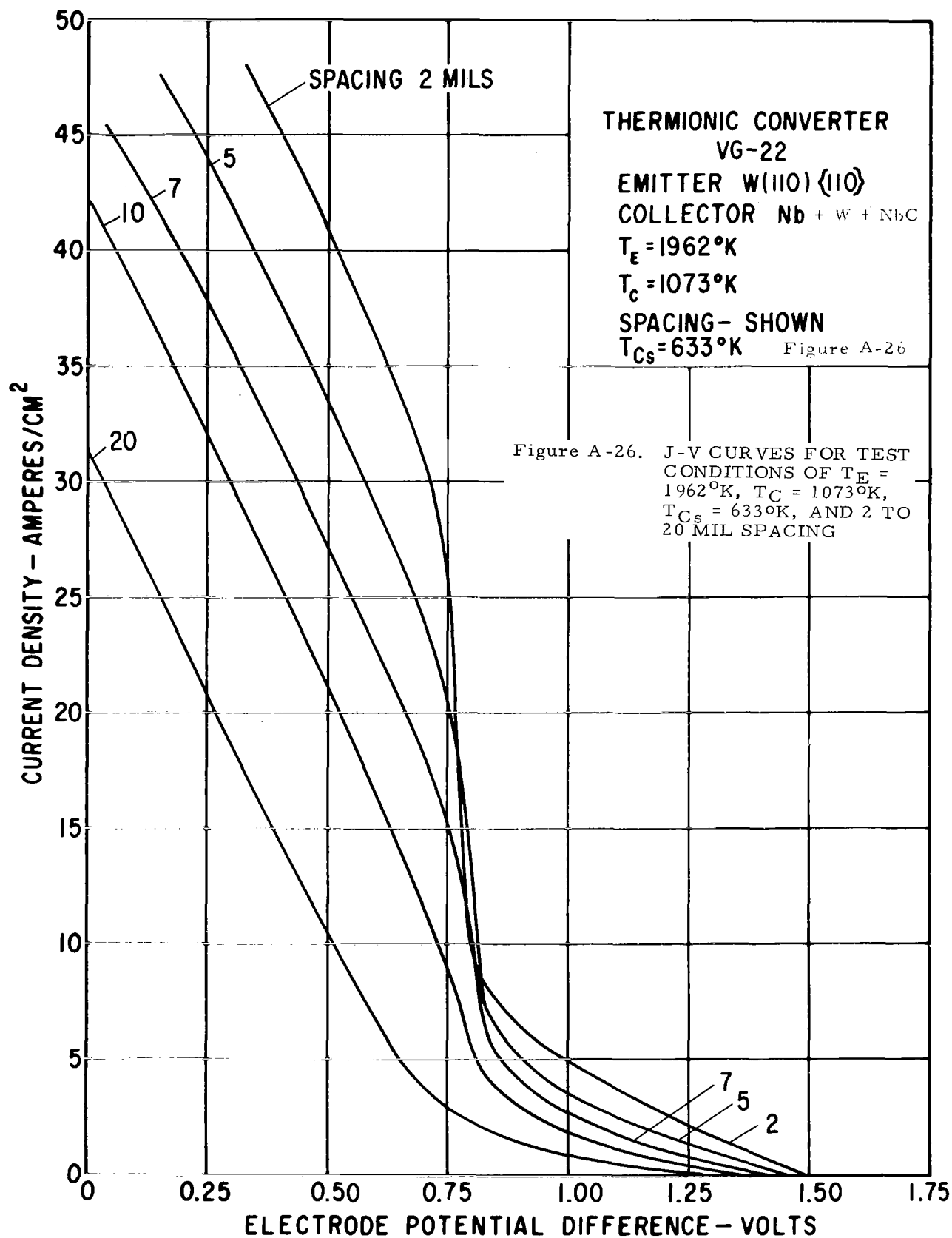


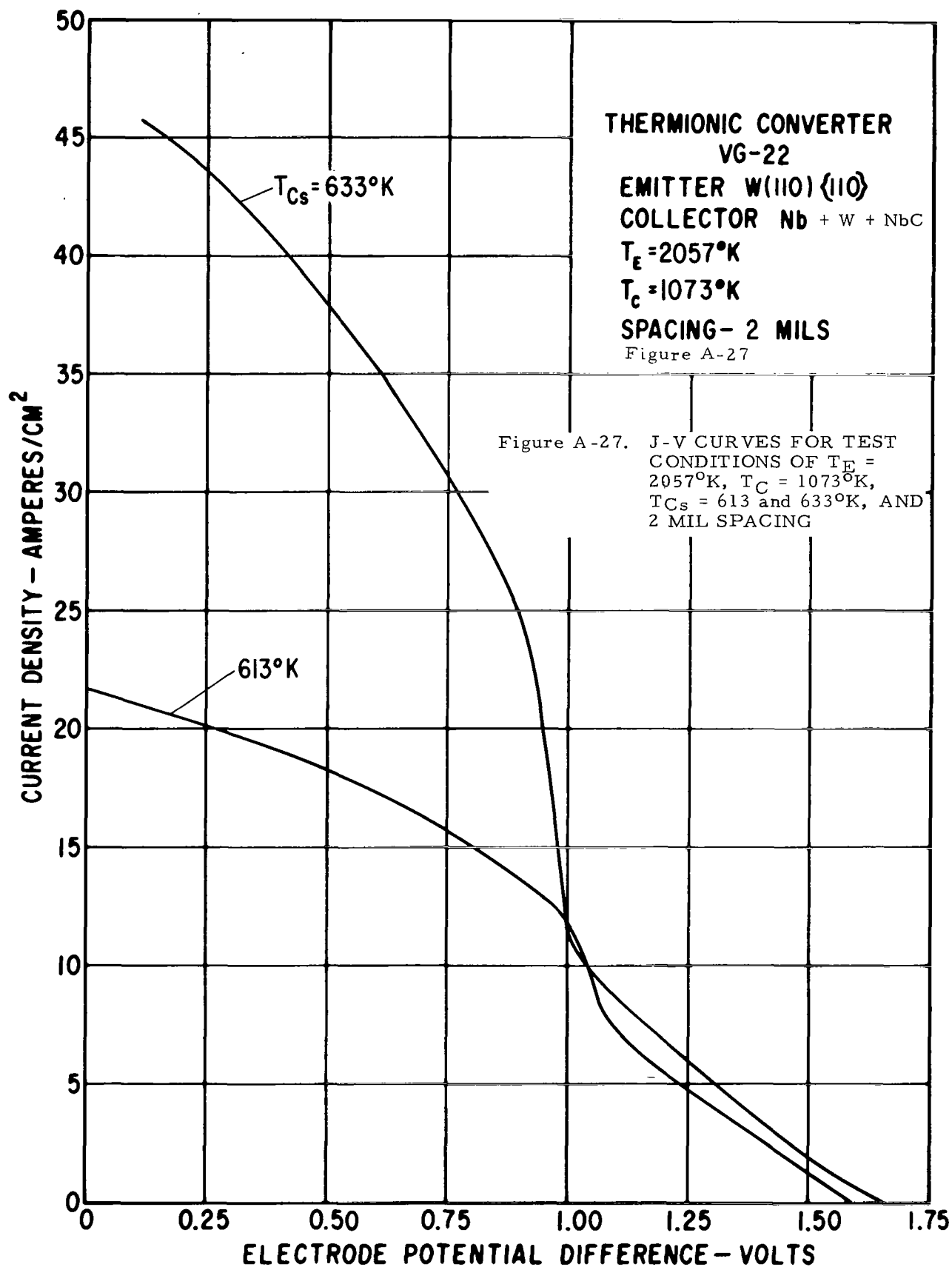


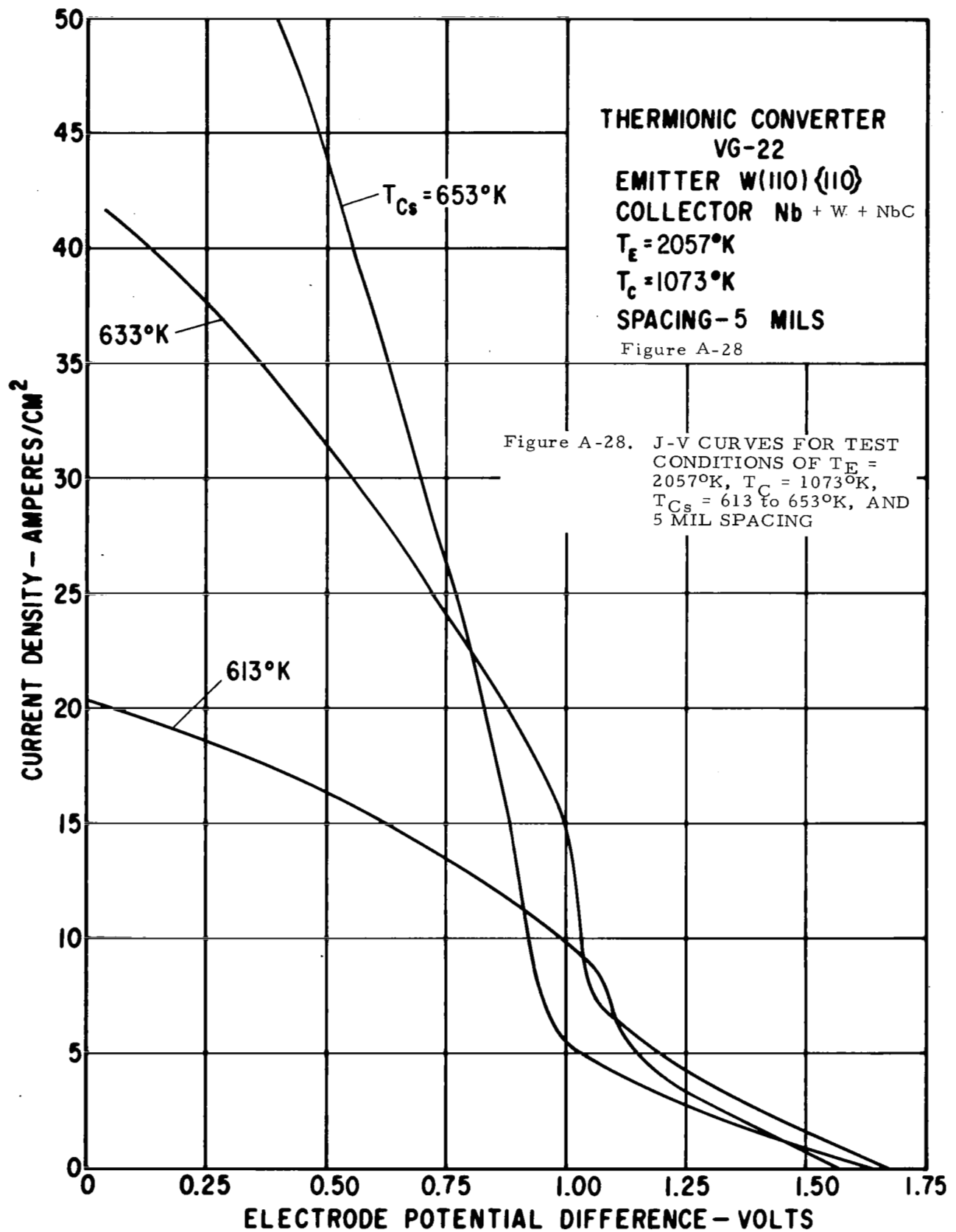


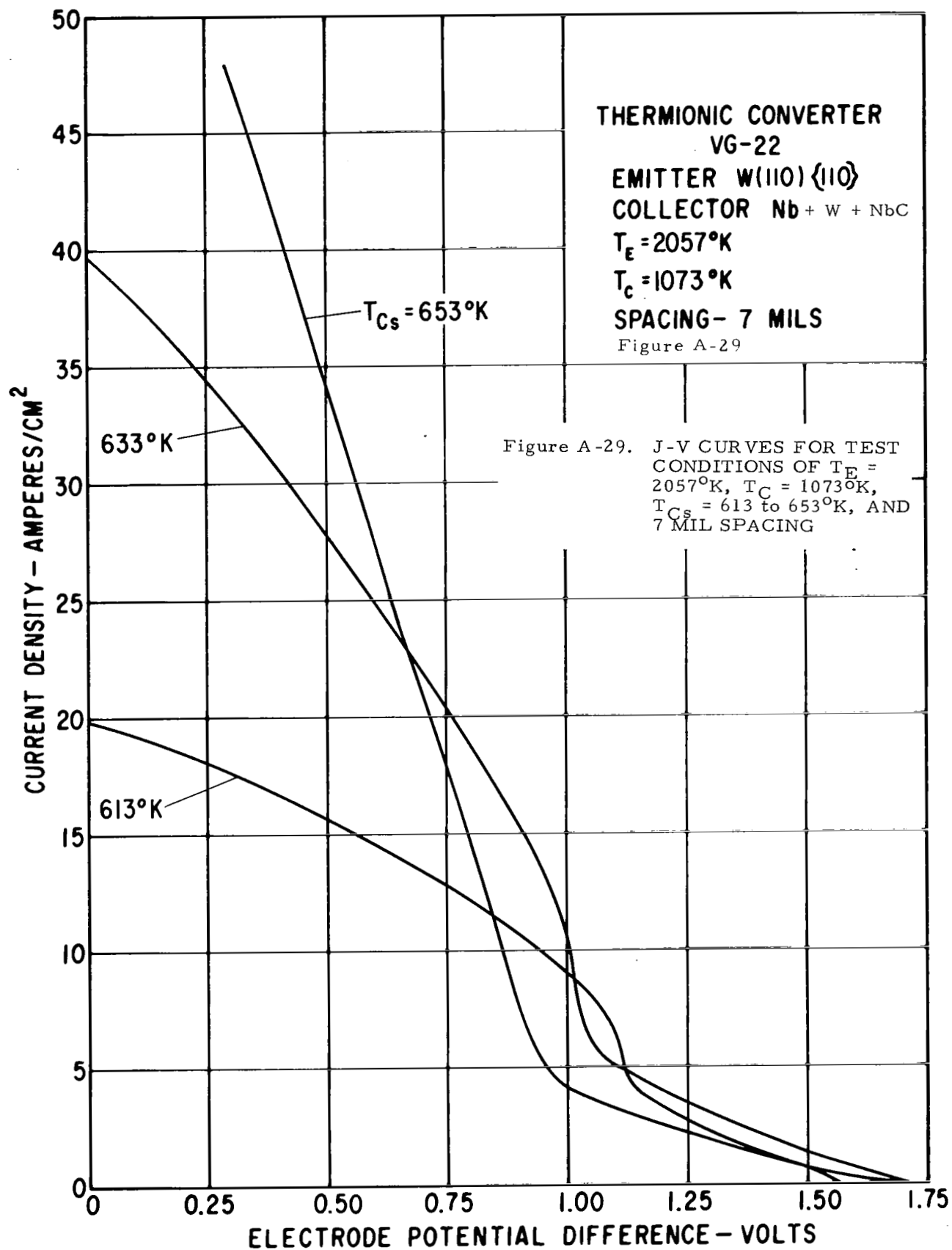


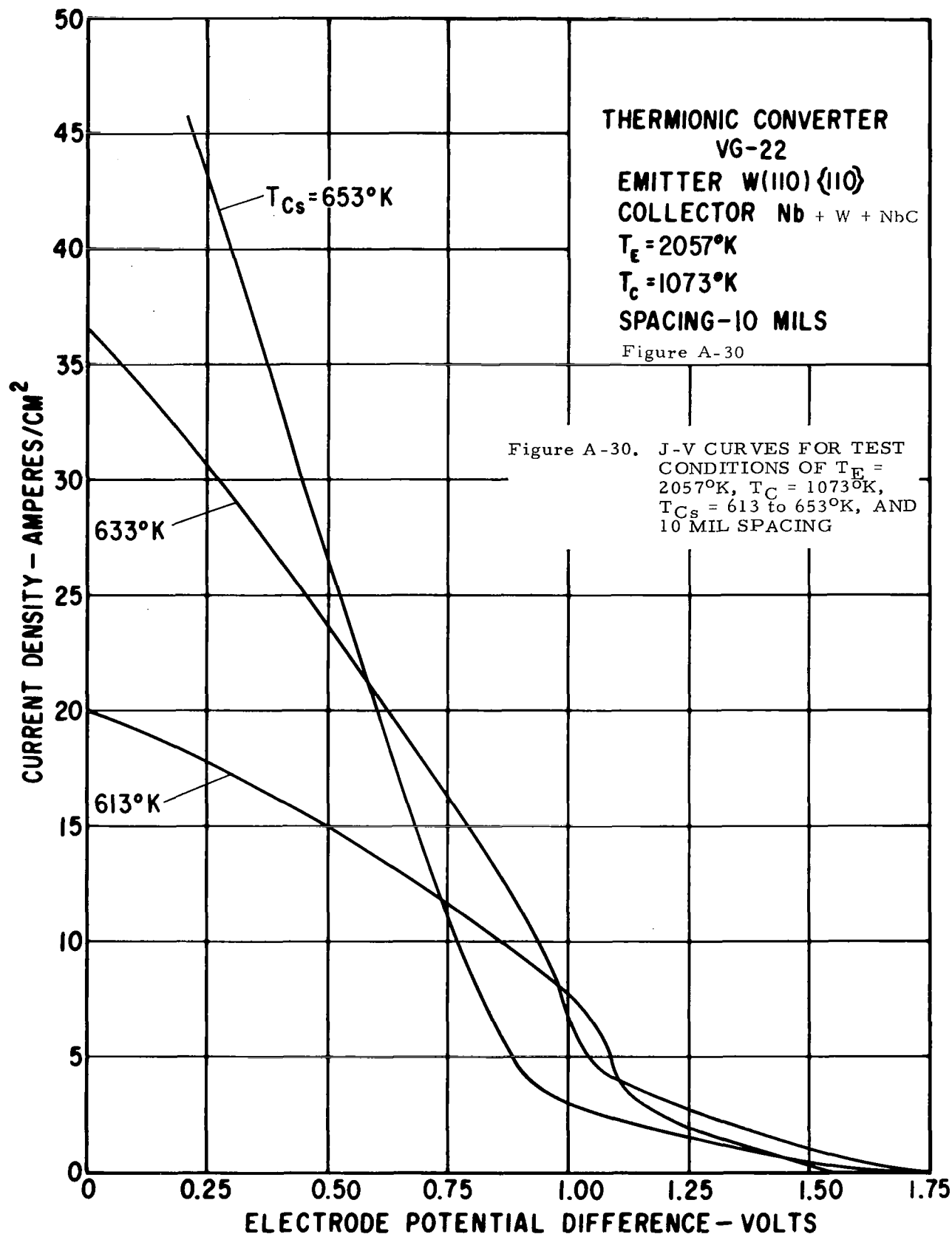


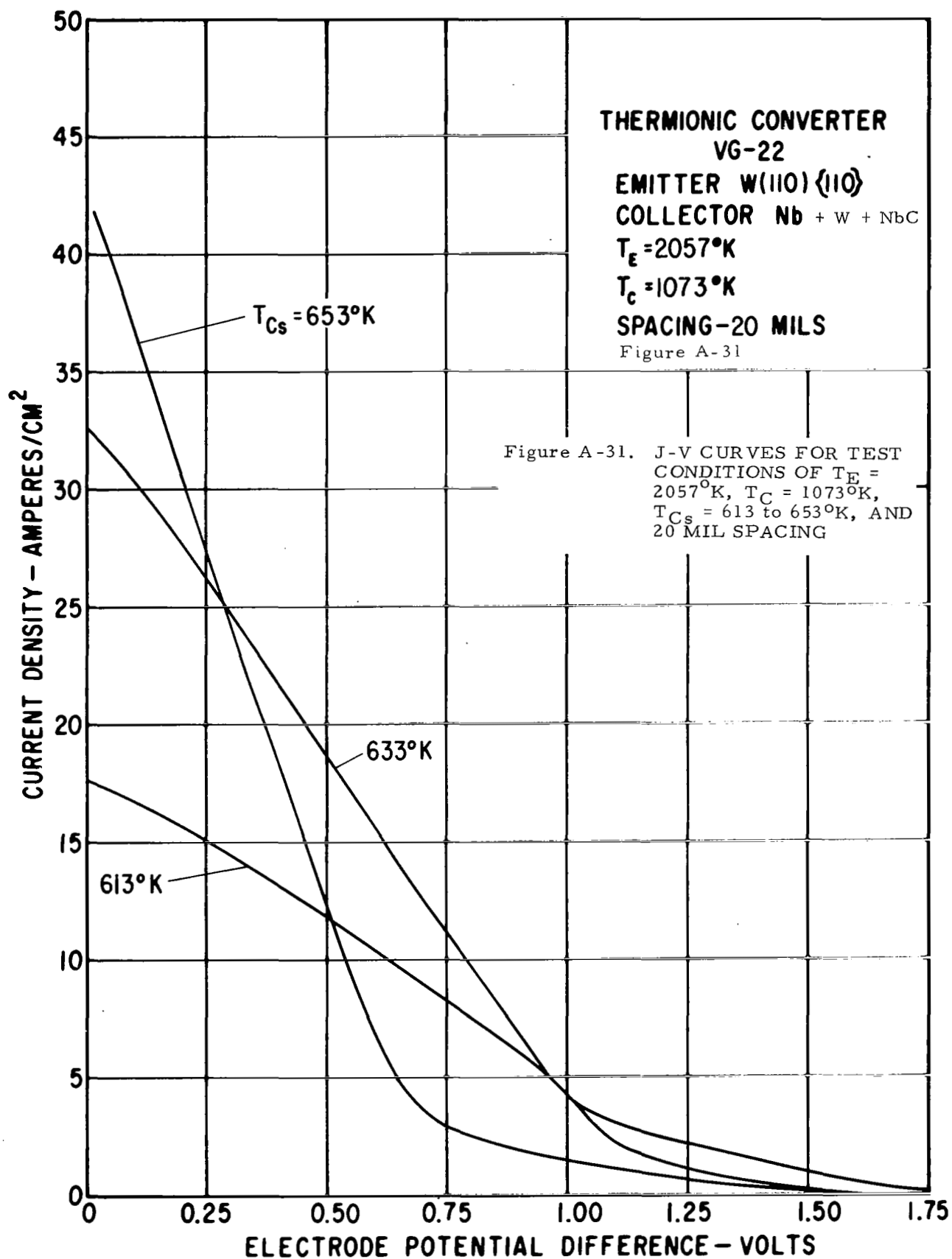


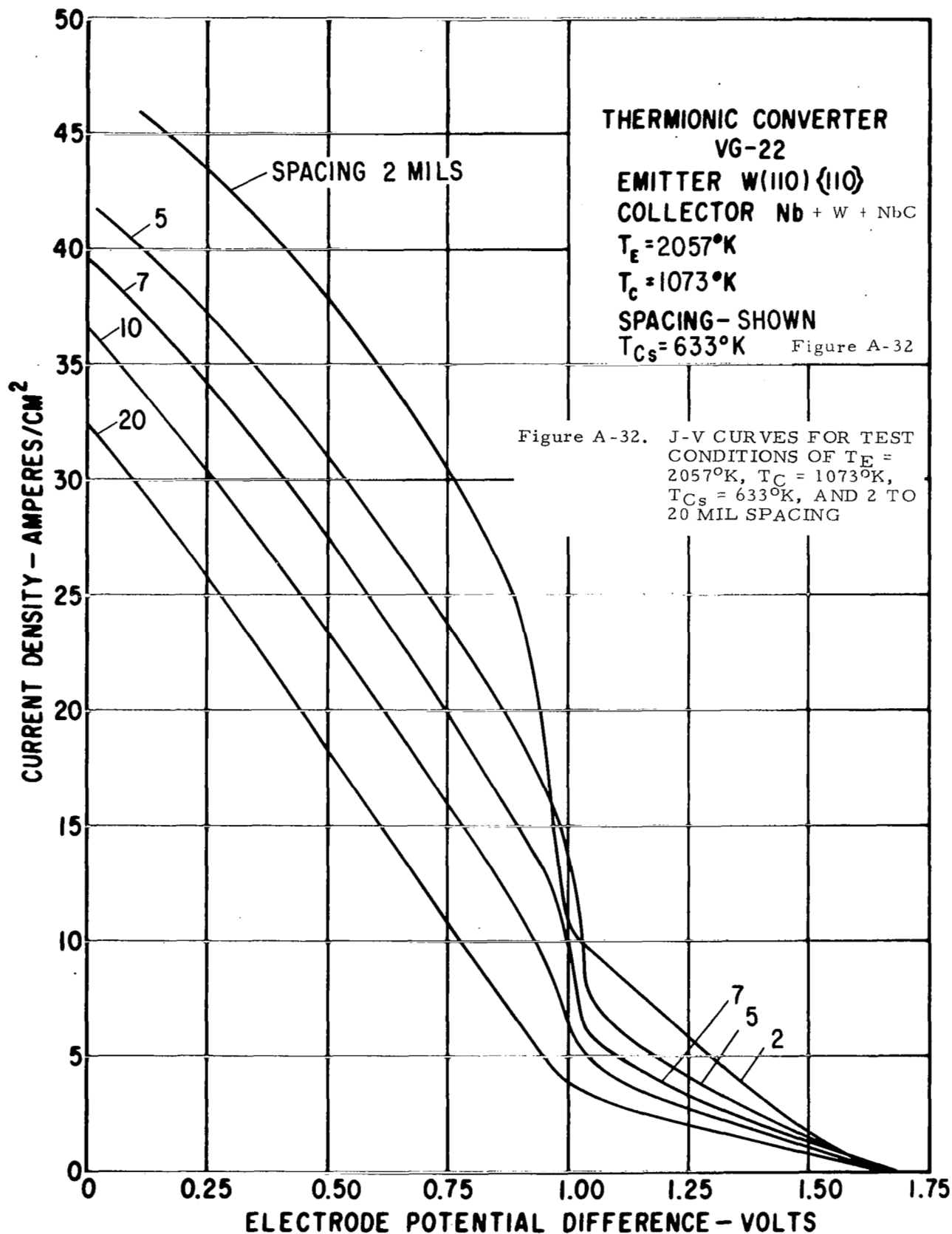


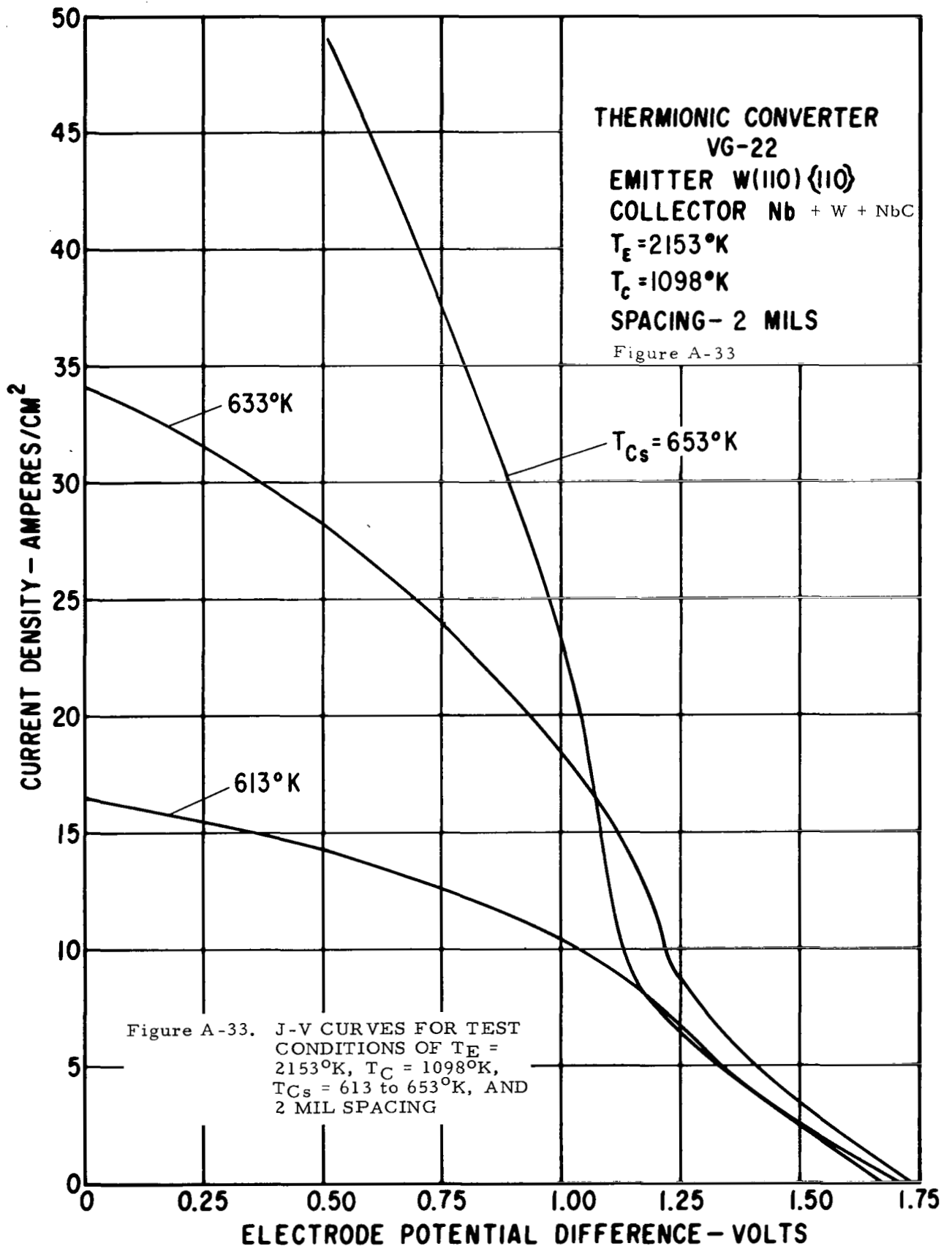


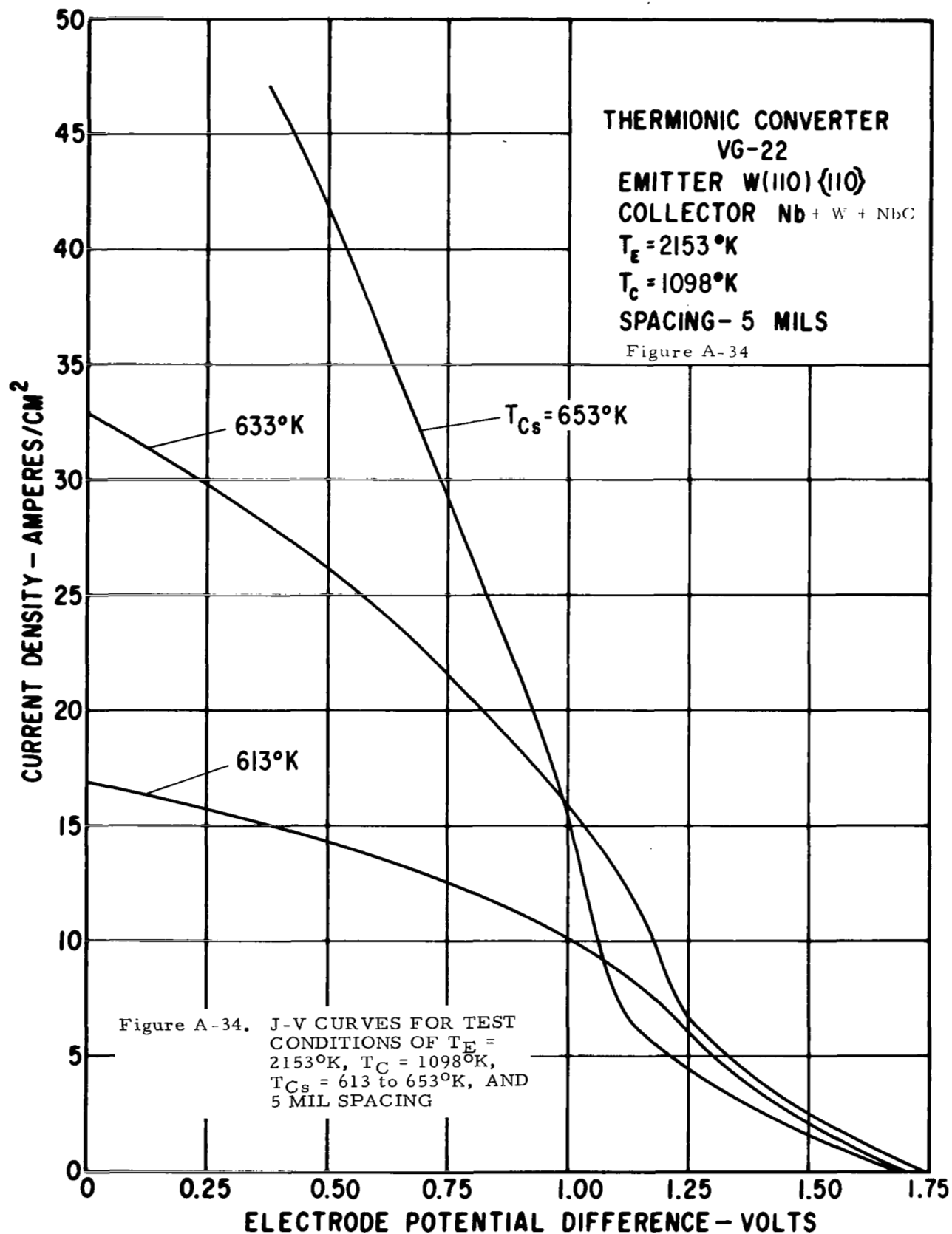


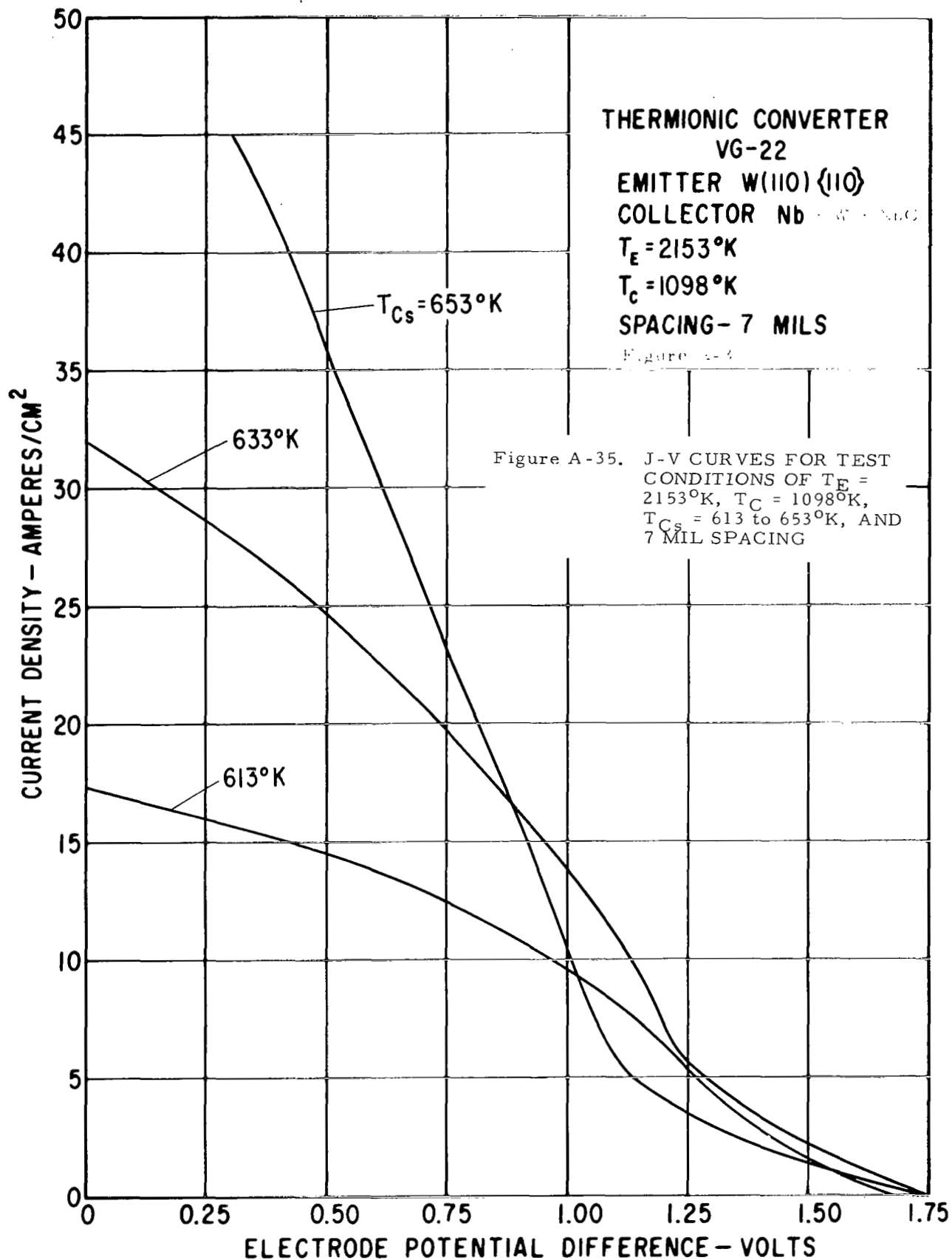


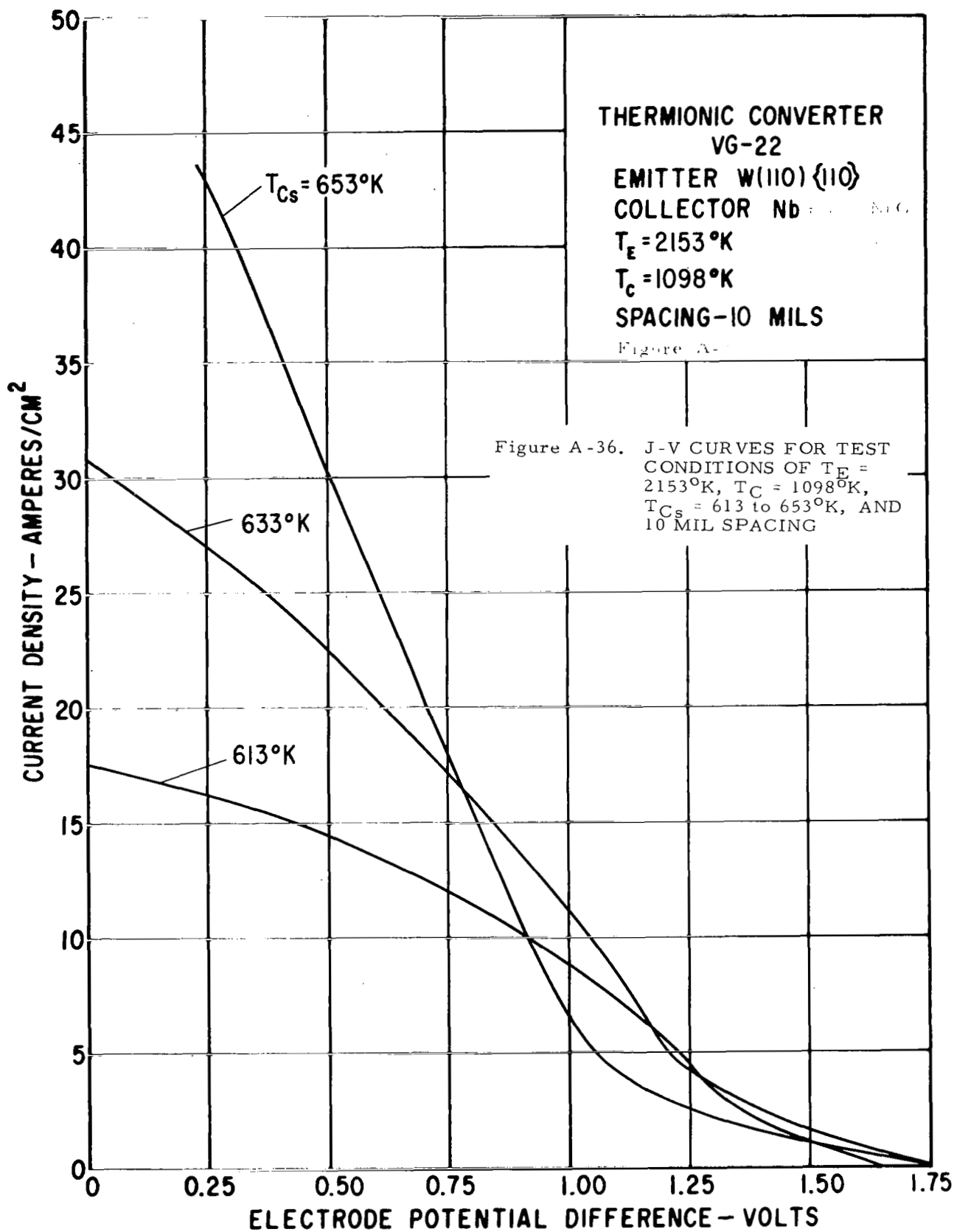


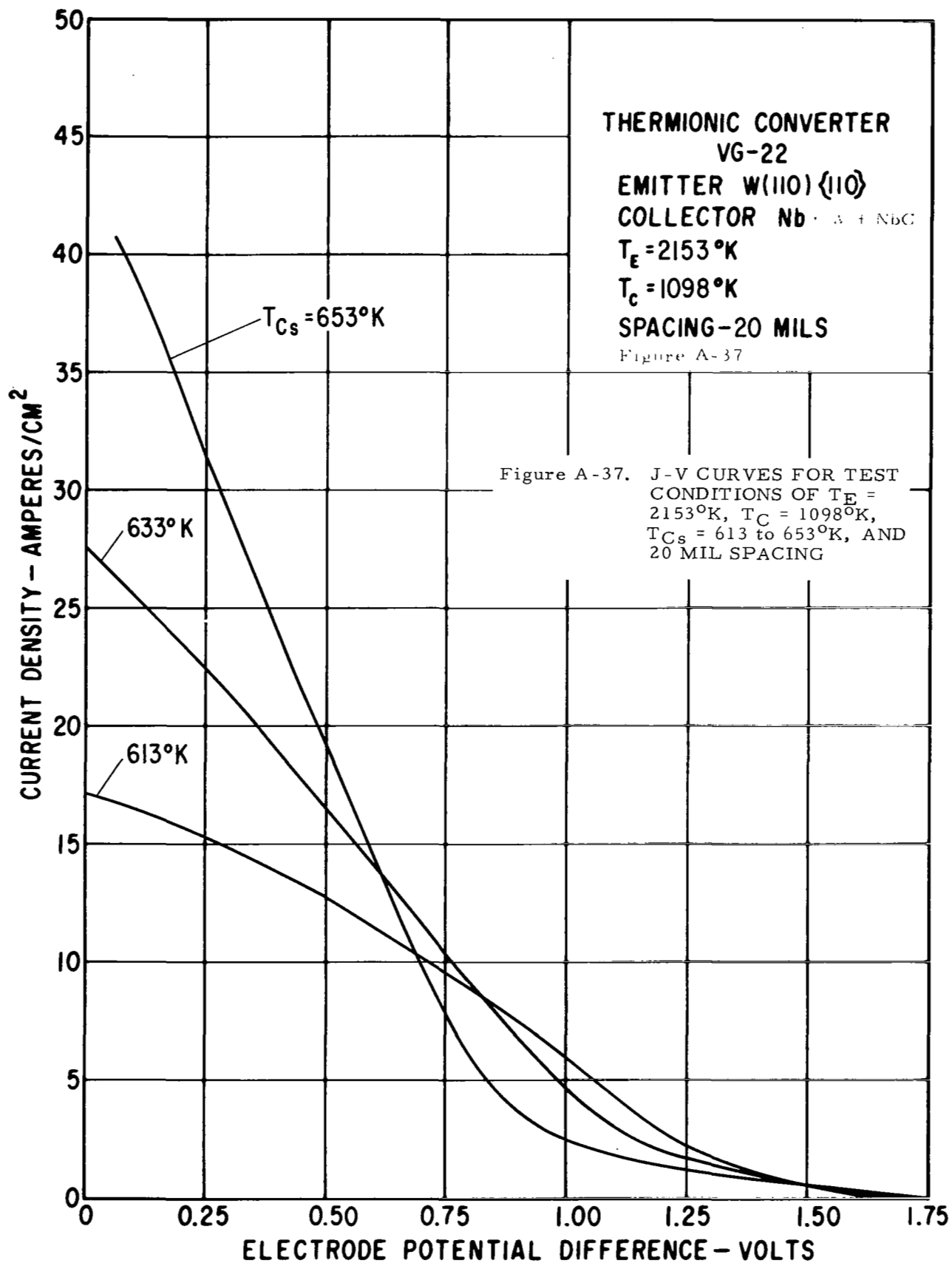


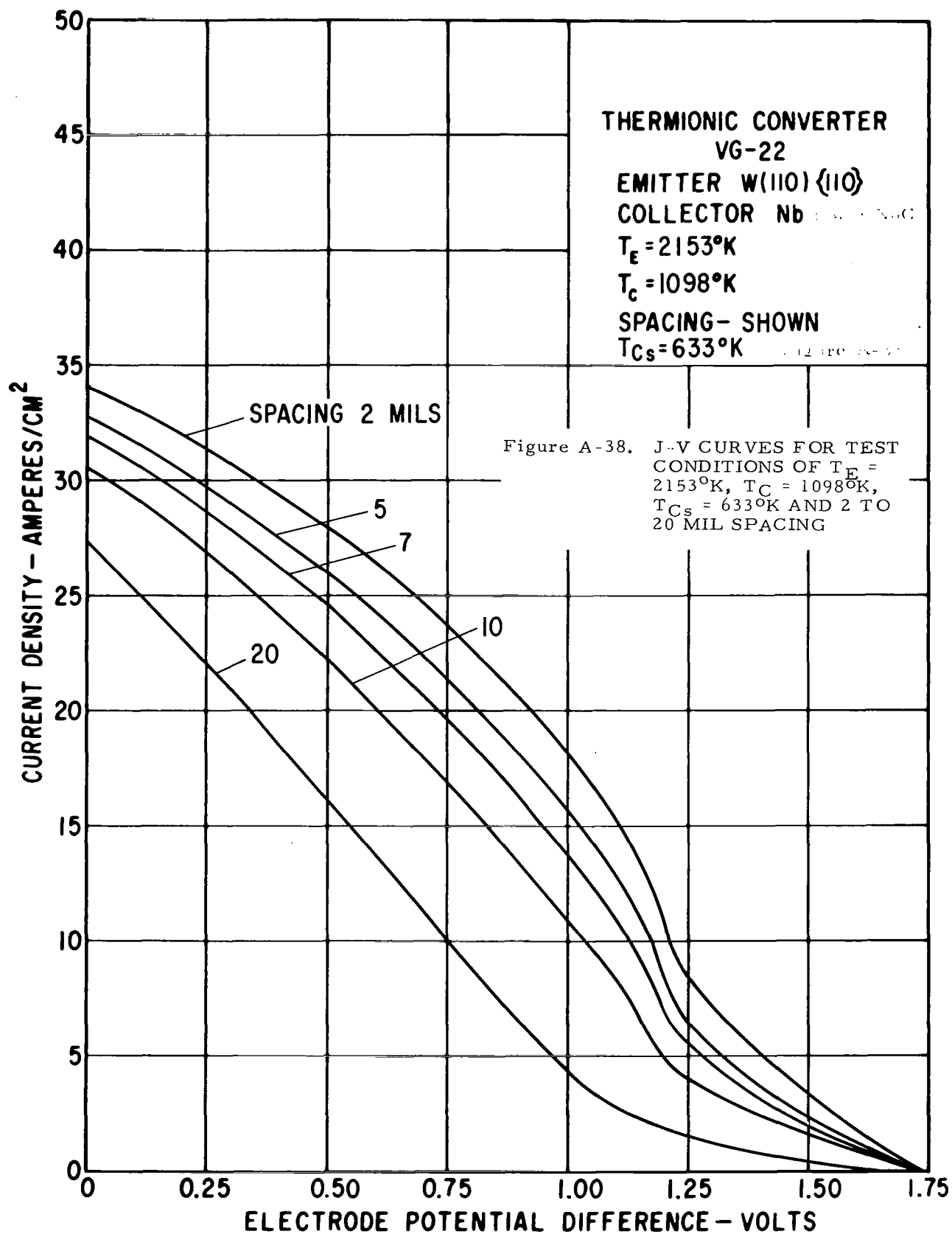












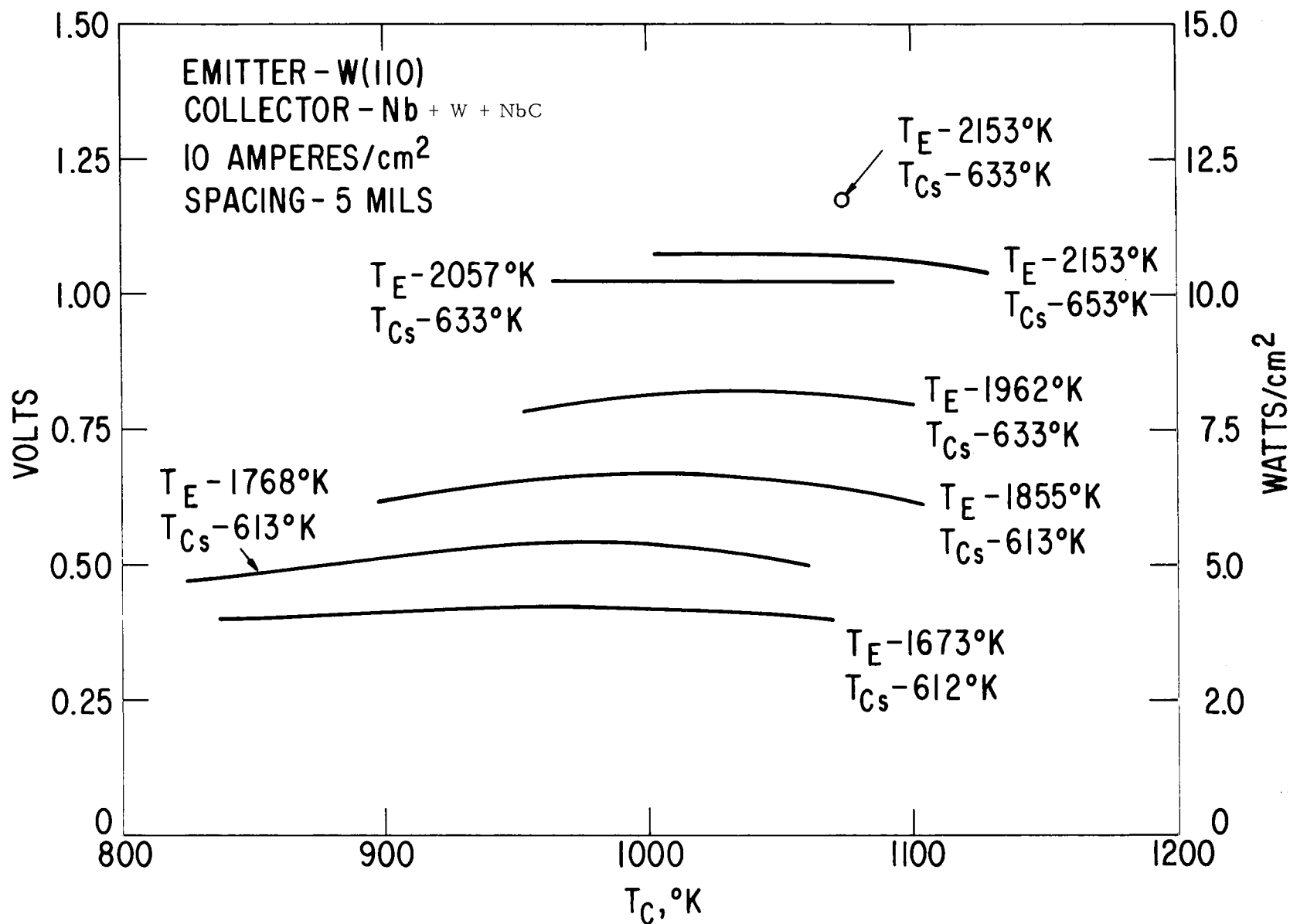


Figure A-39. J-V CURVES FOR TEST CONDITIONS OF $T_E = 1673$ to 2153°K , $T_C = 848$ to 1123°K , $T_{Cs} = \text{various}$, and 5 MIL SPACING

